Synthesis, Structure, and Reactivity of Ruthenium Carboxylato and 2-Oxocarboxylato Complexes Bearing the Bis(3,5-dimethylpyrazol-1-yl)acetato Ligand

Stefan Tampier,†‡ Rainer Müller,‡§ Andrea Thorn,† Eike Hübner,† and Nicolai Burzlaff*,†

Inorganic Chemistry, Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), University of Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Germany, and Department of Chemistry, University of Konstanz, Fach M728, D-78457 Konstanz, Germany

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A series of ruthenium(II) acetonitrile, pyridine (py), carbonyl, SO2, and nitrosyl complexes \([\text{Ru(bdmpza)}(O_2CR)(L)(PPh_3)](L = \text{NCMe}, \text{py}, \text{CO}, \text{SO}_2)\) and \([\text{Ru(bdmpza)}(O_2CR)(L')(PPh_3)]\text{BF}_4(L' = \text{NO})\) containing the bis(3,5-dimethylpyrazol-1-yl)acetato (bdmpza) ligand, a \(N,N,O\) heteroscorpionate ligand, have been prepared. Starting from ruthenium chlorido, carboxylato, or 2-oxocarboxylato complexes, a variety of acetonitrile complexes \([\text{Ru(bdmpza)}\text{Cl(NCMe)}(PPh_3)](4)\) and \([\text{Ru(bdmpza)}(O_2CR)(NCMe)(PPh_3)](5a)\), \(R = \text{Me}(5b)\), \(\text{Ph}(5b)\), \((\text{CO})\text{Me}(8a)\), \((\text{CO})\text{Et}(8b)\), \((\text{CO})\text{Ph}(8c)\)), as well as the pyridine complexes \([\text{Ru(bdmpza)}\text{Cl(PPh_3)(py)}](6)\) and \([\text{Ru(bdmpza)}(O_2CR)(PPh_3)(py)](7a)\), \(R = \text{Me}(7b)\), \(\text{Ph}(7b)\), \((\text{CO})\text{Me}(8a)\), \((\text{CO})\text{Et}(8b)\), \((\text{CO})\text{Ph}(8c)\), have been synthesized. Treatment of various carboxylato complexes \([\text{Ru(bdmpza)}(O_2CR)(PPh_3)2](2a)\), \(\text{Ph}(2b)\) with CO afforded carbonyl complexes \([\text{Ru(bdmpza)}(O_2CR)(\text{CO})(PPh_3)](9a), 9b\)). In the same way, the corresponding sulfur dioxide complexes \([\text{Ru(bdmpza)}(O_2CMe)(PPh_3)(\text{SO}_2)](10a)\) and \([\text{Ru(bdmpza)}(O_2C\text{Ph})(PPh_3)(\text{SO}_2)](10b)\) were formed in a reaction of the carboxylato complexes with gaseous SO2. None of the 2-oxocarboxylato complexes \([\text{Ru(bdmpza)}(O_2C(CO)R)(PPh_3)2](3a)\), \(R = \text{Me}(3b)\), \(\text{Et}(3b)\), \(\text{Ph}(3c)\)) showed any reactivity toward CO or SO2, whereas the nitrosyl complex cations \([\text{Ru(bdmpza)}(O_2C\text{Me})(\text{NO})(PPh_3)]^+\)(11) and \([\text{Ru(bdmpza)}(O_2C(CO)\text{Ph})(\text{NO})(PPh_3)]^+\)(12) were formed in a reaction of the acetato \(2a\) or the benzoylformato complex \(3c\) with an excess of nitric oxide. Similar cationic carboxylato nitrosyl complexes \([\text{Ru(bdmpza)}(O_2CR)(\text{NO})(PPh_3)]\text{BF}_4(13a)\), \(R = \text{Ph}(13b)\)) and 2-oxocarboxylato nitrosyl complexes \([\text{Ru(bdmpza)}(O_2C(CO)R)(\text{NO})(PPh_3)]\text{BF}_4(14a)\), \(R = \text{Me}(14b)\), \(\text{Et}(14b)\), \(\text{Ph}(14c)\)) are also accessible via a reaction with NO\(\text{BF}_4\). X-ray crystal structures of the chlorido acetonitrile complex \([\text{Ru(bdmpza)}\text{Cl(NCMe)}(PPh_3)](4)\), the pyridine complexes \([\text{Ru(bdmpza)}(O_2CMe)(\text{PPh_3})(\text{py})](7a)\) and \([\text{Ru(bdmpza)}(O_2C\text{CO}(\text{Et})(\text{PPh_3})(\text{py})](8b)\), the carbonyl complex \([\text{Ru(bdmpza)}(O_2C\text{Ph})(\text{CO})(\text{PPh_3})](9b)\), the sulfur dioxide complex \([\text{Ru(bdmpza)}(O_2C\text{Ph})(\text{SO}_2)(\text{PPh_3})](10b)\), as well as the nitrosyl complex \([\text{Ru(bdmpza)}(O_2C\text{CO})\text{Me})(\text{NO})(PPh_3)]\text{BF}_4(14a)\), are reported. The molecular structure of the sulfur dioxide complex \([\text{Ru(bdmpza)}(O_2C\text{Ph})(\text{PPh_3})(\text{SO}_2)](10b)\) revealed a rather unusual intramolecular \(\text{SO}_2\text{—O}_2\text{CPh} \text{Lewis acid—base adduct.}

Introduction

Bis(pyrazol-1-yl)acetic acids, such as bis(3,5-dimethylpyrazol-1-yl)acetate (Hbdmpza) introduced 1999 by A. Otero,1 are available in a broad spectrum of chiral and achiral ligands and thus have been subject of two very recent reviews by Otero and Pettinari.1,2 Complexes of these \(N,N,O\) donor ligands with various transition metal complexes reveal their potential in organometallic and coordination chemistry as scorpionate ligands closely related to Tp.1,2 Lately, we reported on ruthenium(II) complexes bearing the bdmpza

* To whom correspondence should be addressed. E-mail: burzlaff@chemie.uni-erlangen.de. Phone: +49(0)9131/85-28976. Fax: +49(0)9131/85-27387.
† University of Erlangen-Nürnberg.
‡ Both authors contributed equally to this work.
§ University of Konstanz.

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ligand such as [Ru(bdmpza)Cl(PPh₃)] (1). Because of the sterical hindrance of the bdmpza ligand, one of the PPh₃ ligands and the chlorido ligand can easily be exchanged for carboxylato or cumulynidene ligands. Other ruthenium complexes bearing the bdmpza ligand have recently been reported by Cao and Otero. The carboxylato complexes [Ru(bdmpza)(O₂C(CO)R)-]

Experimental Section

All experiments were carried out with Schlenk technique under an argon atmosphere. Solvents were dried by distillation over argon. Solvents were dried by distillation over ligands.3 As a proof for these hemilabile ligands, we recently reported by Cao and Otero.5 The carboxylato complexes should be mentioned.7 Therefore, here we study ruthenium(II) complexes with hemilabile ligands, as well as with coordinated solvent molecules, are often key compounds in inorganic syntheses or catalytic reactions. A recent example is the ruthenium hydridotris(pyrrozyl)borate (Tp) complex [RuTpH(NCMe)(PPh₃)], which exhibits catalytic activity for the hydrogenation of CO₂ to formic acid and is easily derived from [RuTpCl(NCMe)(PPh₃)].6 Thus, inspired by [RuTpCl(PPh₃)(MeCN)] we decided to study the coordination of acetonitrile and pyridine by various ruthenium(II) complexes bearing the bdmpza ligand. Furthermore, 16 VE complex fragments coordinating small molecules often allow the synthesis and stabilization of otherwise highly reactive molecules in the complex environment. As an example the synthesis of sulfene complexes starting from ruthenium SO₂ complexes should be mentioned.7 Therefore, here we study also the coordination of small molecules CO, NO, and especially SO₂ that might act as activity for the hydrogenation of CO₂ to formic acid and is an argon atmosphere. Solvents were dried by distillation over ligands.3

δ values are given relative to TMS (1H), solvent peaks (13C) or to 1.I R σ

Method A: General Procedure for the Syntheses of Acetonitrile Complexes. The chlorido, acetato, or benzoato complexes 1, 2a, or 2b were dissolved in acetonitrile, and the reaction mixture was stirred at ambient temperature. The progress of the reaction was monitored by IR spectroscopy. After the reaction was completed, the solvent was reduced in vacuo until precipitation occurred. Precipitation was completed by adding pentane. The product was filtered off and dried in vacuo.


δ values are given relative to TMS (1H), solvent peaks (13C) or to triphenylphosphine at -4.72 ppm as internal standard (31P). FAB MS; modified Finnigan MAT 312. Elemental analyses: Analytical Laboratory of the Department of Chemistry, University of Konstanz or Euro EA 3000 (Euro Vector) and EA 1108 (Carlo Erba) (δ ± 1% of the measured content). A modified Siemens P4 and an Enraf-Nonius CAD 4 Mach 3 diffractometer were used for X-ray structure determination. The syntheses of [Ru(bdmpza)(Cl)(PPh₃)] (1), the ruthenium carboxylato complex [Ru(bdmpza)(O₂C(CO)R)(PPh₃)] (2a) (R = R = Me, 2b: R = Ph) and the ruthenium 2-oxocarboxylato complexes [Ru(bdmpza)(O₂C(O)R)(PPh₃)] (3a: R = Me, 3b: R = Ph, 3c: R = Et, 3d: R = CH₃CH₂CO₂H) were reported recently.3 To remove last traces of thallous carboxylate the aceto and benzoato complexes 2a and 2b were recrystallized from CH₃Cl/pentane. All the 2-oxocarboxylato complexes used for experiments had been synthesized by using this crystalline complex 2a. Acetonitrile and pyridine have been distilled prior to use. Nitrogen oxide, carbon monoxide, carbon dioxide, nitrogen and sulfur dioxide were used as purchased. For differentiation of the NMR data the signals of the bdmpza ligand next to the PPh₃ ligand are marked without an apostrophe.
[Ru(bdmpza)(O2CMe)(N(Me)(PPh3))] (5a) as a yellow crystalline powder.

Yield 0.141 g (0.198 mmol, 99%). mp 145 °C (dec.). IR (CH2Cl2): ν = 2271 w (C≡N), 1663 vs (CO2), 1648 sh, 1608 m, 1591 sh, 1564 w (C≡N), 1484 w, 1464 v, 1434 m, 1417 vw cm⁻¹. IR (KBr): ν = 2263 w (C≡N), 1659 vs (CO2), 1606 s, 1587 sh, 1564 w (C≡N), 1483 w, 1463 v, 1434 m, 1417 vw cm⁻¹. UV/vis (CH2Cl2): λmax/ν (log ε) = 2360.4 (4.36), 2680.0 (3.74), 2750.3 (3.75), 3040.0 (3.76), 3620.0 (3.71). FAB-MS (NBOOH-matrix): m/z (%) = 711 (8) [M⁺], 651 (97) [M⁺ − HO2CMe], 610 (100) [M⁺ − HO2CMe − MeCN], 565 (46) [M⁺ − HO2CMe − CO2 − MeCN − H⁺]. 1H NMR (CDCl3, 400 MHz): δ = 1.31 (s, 3H, OAc-CH3), 1.56 (s, 3H, C3-CH3), 2.22 (s, 3H, NC-CH3), 2.43 (s, 3H, C12-CH3), 2.47 (s, 3H, C11-CH3), 2.54 (s, 3H, C3-CH3), 5.91 (s, 1H, Hpz), 6.07 (s, 1H, Hpz), 6.55 (s, 1H, CH), 7.10−7.50 (m, 15H, PPh3) ppm. FAB-MS (NBOOH-matrix): m/z (%) = 724 (7) [M⁺], 647 (7) [M⁺ − Py], 460 (6) [M⁺ − PPh3], 363 (6) [M⁺ − Cl − Py − bmdpza], 217 (100) [M⁺ − PPh3 − bmdpza]. 13C NMR (CDCl3, 100 MHz): δ = 170.0 (s, C3-CH3), 174.8 (C35H35ClN5O2PRu (725.19): C, 57.97; H, 4.86; N, 9.66. Found: C, 57.81; H, 4.99; N, 8.96. 

Method B: General Procedure for the Syntheses of Pyridine Complexes. To a solution of the chlorido, carboxylato, or oxo-acetylato complexes 1, 2a, 2b, and 3a−c in dichloromethane was added pyridine. The reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by IR spectroscopy. After the reaction was completed, the solvent was reduced in vacuo, and the product was precipitated with n-pentane. The precipitate was filtered off and dried in vacuo.

[Bu(bdmpza)(O2CMe)(N(Me)(PPh3))] (7a) as an orange microcrystalline powder.

Yield 0.266 g (0.355 mmol, 86%). mp 200 °C (dec.). IR (CHCl3): ν = 1663 vs (CO2), 1619 s, 1567 w (C≡N), 1482 m, 1464 vw, 1448 w, 1434 m, 1420 vw cm⁻¹. IR (KBr): ν = 2263 w (C≡N), 1651 vs (CO2), 1605 s, 1570 s (C≡N), 1484 w, 1464 vw, 1434 m, 1419 vw cm⁻¹. UV/vis (CH2Cl2): λmax/ν (log ε) = 2380.4 (3.33), 2680.0 (3.94), 2750.3 (3.93), 2960.0 (3.93). FAB-MS (NBOOH-matrix): m/z (%) = 773 (3) [M⁺], 731 (100) [M⁺ − MeCN], 651 (29) [M⁺ − O2CPh], 610 (43) [M⁺ − O2CPh − MeCN]. Isomer A: 1H NMR (CDCl3, 600 MHz): δ = 1.61 (s, 3H, C3-CH3), 2.23 (s, 3H, NC-CH3), 2.30 (s, 3H, C12-CH3), 2.51 (s, 3H, C11-CH3), 2.57 (s, 3H, C12-CH3), 5.93 (s, 1H, Hpz), 6.01 (s, 1H, Hpz), 6.62 (s, 1H, CH), 7.05−7.65 (m, 20H, Ph and PPh3) ppm. 13C NMR (CDCl3, 150.9 MHz): δ = 2.23 (NC3H11), 11.0 (C12CH3), 11.6 (C12CH3), 13.3 (C12CH3), 14.2 (C12-CH3), 164.3 (CO2), 179.7 (OAc-CO2) ppm. 31P NMR (CDCl3, 161.8 MHz): δ = 53.4 ppm. Anal. Calcd for C35H35ClN5O2PRu × H2O: C, 52.85; H, 4.91; N, 8.89. Found: C, 52.85; H, 4.90; N, 8.89.
7.10 (OAc·COO −) ppm. 13C NMR (CDCl3, 100.5 MHz): δ = 11.2 (C3-CH3), 11.5 (C5-CH3), 11.5 (C7-CH3), 14.2 (C7′-CH3), 24.8 (OAc·CH3), 69.2 (CH), 107.9 (d, C2′-CH3, δC = 2.8 Hz), 108.1 (C3), 122.6 (m-py′), 123.2 (m-py′), 127.4 (d, m-PPh3, δC = 8.8 Hz), 128.7 (s-PPh3), 133.7 (p-py), 133.9 (br, o-PPh3), 134.9 (d, i-PPh3, JCP = 83.8 Hz), 139.9 (C5′), 141.1 (C5), 153.9 (d, C′, δC′ = 2.8 Hz), 154.4 (o-py), 155.4 (o′-py), 157.7 (C′′), 168.4 (CO2), 171.1 (CO·CO2), 197.6 (C=C=O) ppm. 31P NMR (CDCl3, 161.8 MHz; δ = 49.7 ppm. Anal. Calc. For C51H43N10O4P2Ru (776.79): C, 58.76; H, 4.93; N, 9.02. Found: C, 58.42; H, 5.20; N, 8.76.

[Ru(bdpmpz)(O2CC(O)Et)(PPh3)(py)] (8b). Reaction of [Ru(bdpmpz)(O2CC(O)Et(PPh3)] (3b) (0.269 g, 0.378 mmol) in CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)Et)(PPh3)] (8b) as an orange crystalline powder. Crystals suitable for X-ray structure determination were obtained from a CH2Cl2 solution layered with n-hexane.

Yield 0.209 g (0.264 mmol, 70%). mp 210 °C (dec.). IR (CH2Cl2): 7.50 (m, 1H, Ph and PPh3), 7.98 (t, 1H, Hpz), 8.05 (br, CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)PPh3)(py)] (7b) as yellow powder.

Yield 0.265 g (0.327 mmol, 92%), mp 220 °C (dec.). IR (CH2Cl2): ν = 1659 vs (CO2), 1636 w, 1626 w, 1618 w, 1575 m (C=C), 1568 w, 1482 m, 1464 v, 1447 v, 1434 w, 1420 vw cm−1. IR (KBr): 7.50 (m, 1H, Ph and PPh3), 7.98 (t, 1H, Hpz), 8.05 (br, CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)PPh3)(py)] (7b) as yellow powder.

Yield 0.265 g (0.327 mmol, 92%), mp 220 °C (dec.). IR (CH2Cl2): ν = 1659 vs (CO2), 1636 w, 1626 w, 1618 w, 1575 m (C=C), 1568 w, 1482 m, 1464 v, 1447 v, 1434 w, 1420 vw cm−1. IR (KBr): 7.50 (m, 1H, Ph and PPh3), 7.98 (t, 1H, Hpz), 8.05 (br, CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)PPh3)(py)] (7b) as yellow powder.

Yield 0.265 g (0.327 mmol, 92%), mp 220 °C (dec.). IR (CH2Cl2): ν = 1659 vs (CO2), 1636 w, 1626 w, 1618 w, 1575 m (C=C), 1568 w, 1482 m, 1464 v, 1447 v, 1434 w, 1420 vw cm−1. IR (KBr): 7.50 (m, 1H, Ph and PPh3), 7.98 (t, 1H, Hpz), 8.05 (br, CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)PPh3)(py)] (7b) as yellow powder.

Yield 0.265 g (0.327 mmol, 92%), mp 220 °C (dec.). IR (CH2Cl2): ν = 1659 vs (CO2), 1636 w, 1626 w, 1618 w, 1575 m (C=C), 1568 w, 1482 m, 1464 v, 1447 v, 1434 w, 1420 vw cm−1. IR (KBr): 7.50 (m, 1H, Ph and PPh3), 7.98 (t, 1H, Hpz), 8.05 (br, CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)PPh3)(py)] (7b) as yellow powder.

Yield 0.265 g (0.327 mmol, 92%), mp 220 °C (dec.). IR (CH2Cl2): ν = 1659 vs (CO2), 1636 w, 1626 w, 1618 w, 1575 m (C=C), 1568 w, 1482 m, 1464 v, 1447 v, 1434 w, 1420 vw cm−1. IR (KBr): 7.50 (m, 1H, Ph and PPh3), 7.98 (t, 1H, Hpz), 8.05 (br, CH2Cl2 (15 mL) with pyridine (0.302 g, 3.82 mmol) for 3 days according to method B afforded [Ru(bdpmpz)(O2CC(O)PPh3)(py)] (7b) as yellow powder.
Method C: General Procedure for Complex Syntheses with Gaseous CO, SO₂, and NO. A solution of the acetato, benzoato, or benzyloximate complexes 2a, 2b, or 3c in dichloromethane was flushed with gaseous CO, SO₂, or NO under stirring at ambient temperature. The progress of the reactions was monitored by IR spectroscopy. After the reaction was completed, the solvent was reduced in vacuo, and the product was precipitated with n-pentane.

The precipitate was filtered off and dried in vacuo.

[Ru(bdmpza)(O₂CMe)(PPh₃)] (9a). Reaction of [Ru(bdmpza)(O₂CMe)(PPh₃)] (2a) (275 mg, 0.411 mmol) in CH₂Cl₂ (100 mL) with CO for 2 h according to method C afforded the product [Ru(bdmpza)(O₂CMe)(PPh₃)] (9a) as a yellow powder.

Yield 325 mg (0.404 mmol, 97%). mp 150 °C (dec.). IR (CHCl₃): δ = 1977 vs (CO), 1669 vs (CO₂), 1624 w, 1602 vw, 1564 w (C=O), 1485 vw, 1465 vw, 1437 m, 1419 vw cm⁻¹. IR (KBr): δ = 1967 vs (CO), 1672 vs (CO₂), 1620 m, 1600 vw, 1560 m (C=O), 1481 vw, 1462 vw, 1434 m, 1420 vw cm⁻¹. UV/vis (CH₂Cl₂): 460 max (λ max = 2540 (4.17)). FAB MS (NBOH): m/z (%) = 698 (34 [M⁺ - O₂CMe]), 639 (100) [M⁺ - O₂CMe], 565 (12) [M⁺ - HO₂CMe - CO₂ - CO - H], 391 (41) [M⁺ - bdmpzaH - O₂CMe], 363 (35) [M⁺ - bdmpzaH - O₂CMe - CO]. 'H NMR (CDCl₃, 600 MHz): δ = 1.55 (3H, OAc-Ch₃), 1.91 (3H, C₁⁻CH₃), 2.33 (3H, C₁⁻CH₃), 2.46 (3H, C₁⁻CH₃), 2.55 (3H, C₃⁻CH₃), 6.03 (3H, H₃), 6.04 (3H, H₃), 6.57 (3H, H₃, CH), 7.32 (6H, m-PPh₃), 7.40 (4H, 9- and 10-PPh₃). ¹³C NMR (CDCl₃, 150.9 MHz): δ = 11.3 (C₃⁻CH₃), 11.5 (C₃⁻CH₃), 13.7 (C₃⁻CH₃), 14.0 (C₁⁻CH₃), 22.9 (OAc-Ch₃), 69.3 (CH), 108.6 (C₁⁻CH₃), 109.3 (C₁⁻CH₃), 128.4 (d, m-PPh₃, ²JCP = 9.8 Hz), 130.4 (d, m-PPh₃), 133.1 (d, i-PPh₃, ²JCP = 9.8 Hz), 143.0 (d, i-PPh₃, ²JCP = 9.8 Hz), 140.1 (d, o-PPh₃, ²JCP = 11.3 Hz), 144.8 (C₁⁻CH₃), 154.6 (C₁⁻CH₃), 155.9 (C₁⁻CH₃), 166.3 (OAc-Ch₃), 177.3 (OAc-Ch₃), 205.3 (d, OAc-Ch₃, ²JCP = 19.8 Hz). ³¹P NMR (CDCl₃, 161.8 MHz): δ = 43.3. Anal. Calc. for C₃₉H₃₅N₄O₆P₃Ru: C 60.07; H, 4.64; N, 7.36. Found: C, 59.78; H, 4.79; N, 7.32.

[Ru(bdmpza)(O₂CMe)(PPh₃)(SO₂)] (10a). Reaction of [Ru(bdmpza)(O₂CMe)(PPh₃)] (2a) (654 mg, 0.977 mmol) in CH₂Cl₂ (150 mL) with gaseous SO₂ for 30 min according to method C afforded [Ru(bdmpza)(O₂CMe)(SO₂)(PPh₃)] (10a) as a yellow powder.

Yield 678 mg (0.924 mmol, 95%). mp 180 °C (dec.). IR (CHCl₃): δ = 1673 vs (CO₂), 1566 w (C=O), 1483 vw, 1465 vw, 1436 m, 1419 vw, 1395 vw, 1313 vw, 1284 m, 1128 s, 1094 w, 1091 vw cm⁻¹. IR (KBr): δ = 1672 vs (CO₂), 1566 w (C=O), 1484 vw, 1463 m, 1437 m, 1420 w, 1374 vw, 1352 vw, 1310 vw, 1282 m, 1128 s, 1093 w, 1089 vw cm⁻¹. UV/vis (CH₂Cl₂): λmax (λ max = 246.0) (4.26). FAB MS (NBOH): m/z (%) = 735 (30 [M⁺ + H], 670 (100) [M⁺ + SO₂], 611 (92) [M⁺ - SO₂ - O₂CMe], 565 (27) [M⁺ - SO₂ - CO₂ - HO₂CMe - H], 363 (20) [M⁺ - bdmpzaH - SO₂ - O₂CMe]. 'H NMR (CDCl₃, 250 MHz): δ = 1.77, 1.92, 2.12, 2.43, 2.48 (3H, 15CH₃), 39.1 Hz), 140.9 (C₅), 134.4 (C₃), 154.3 (C₃), 154.3 (PPh₃), 155.8 (o'-PPh₃), 157.8 (C₈), 168.4 (CO₂), 172.5 (O=O), 190.4 (C=O) ppm. ³¹P NMR (CDCl₃, 161.8 MHz): δ = 43.6. Anal. Calc. for C₄₃H₄₀N₅O₅PRu (759.76): C, 60.07; H, 4.64; N, 7.37. Found: C, 59.98; H, 4.79; N, 7.32.
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Yield 848 mg, mp 55–60 °C (dec.). IR (CH2Cl2): ν = 1911 vs (NO), 1698 s, 1564 m (CO2−), 1463 s, 1436 m, 1418,vw cm−1. 1H NMR (CDCl3, 150 MHz): δ = 1.95, 2.36, 2.57, 2.62 (s, 12H, C3−CH3), 2.56, 2.62 (s, 3H, C5−CH3), 6.22, 6.24 (s, 2H, H4aram), 6.71 (s, 1H, CH), 7.30–7.70 (m, 18H, Ph and PPh3), 7.99 (vt, 2H, o-Phe). 13C NMR (CDCl3, 62.9 MHz): δ = 11.1, 11.5, 13.9, 14.3 (C3−CH3), 68.2 (CH1), 110.1 (d, C4 or C4′), 143.5 (C4 or C4′), 120.0 (d or C3−CH3), 131.5 (d, C5−CH3), 127.2 (d or C3−CH3), 168.1 (COOH). 31P NMR (CDCl3, 161.8 MHz): δ = 24.2. Counterion unspecified.

Method D: General Procedure for the Syntheses of NO Complexes from [NO]BF4. A solution of the carboxylato or 2-oxocarboxylato complexes 2a, 2b, or 3a−c in dichloromethane was reacted with [NO]BF4. After 0.5 to 1 h the reaction was completed, the solvent was reduced in vacuo, and the product was precipitated with diethyl ether. The precipitate was filtered off and dried in vacuo.

[Ru(bdpma)(O2CMe)(NO)(PPh3)]BF4 (13a). Reaction of [Ru(bdpma)(O2CMe)(PPh3)] (2a) (533 mg, 0.796 mmol) with [NO]BF4 (175 mg, 1.50 mmol) in CH2Cl2 (40 mL) at ambient temperature afforded after 30 min according to method D the product [Ru(bdpma)(O2CMe)(NO)(PPh3)]BF4 (13a) as a pale red powder.

Yield 593 mg (0.754 mmol, 95%), mp 175 °C (dec.). IR (CH2Cl2): ν = 1912 vs (NO), 1698 s (CO2−), 1635 m (CO2−), 1612 v (CO2−), 1562 m (C=N), 1483 w, 1465 v, 1437 m, 1419 vw cm−1. 1H NMR (CDCl3, 150 MHz): δ = 1.95, 2.36, 2.57, 2.62 (s, 12H, C3−CH3), 2.56, 2.62 (s, 3H, C5−CH3), 6.22, 6.24 (s, 2H, H4aram), 6.71 (s, 1H, CH), 7.30–7.70 (m, 18H, Ph and PPh3), 7.99 (vt, 2H, o-Phe). 13C NMR (CDCl3, 62.9 MHz): δ = 11.1, 11.5, 13.9, 14.3 (C3−CH3), 68.2 (CH1), 110.1 (d, C4 or C4′), 143.5 (C4 or C4′), 120.0 (d or C3−CH3), 131.5 (d, C5−CH3), 127.2 (d or C3−CH3), 168.1 (COOH). 31P NMR (CDCl3, 161.8 MHz): δ = 24.2. Counterion unspecified.

[Ru(bdpma)(O2CC(O)Me)(NO)(PPh3)]BF4 (14a). Reaction of [Ru(bdpma)(O2CC(O)Me)(PPh3)] (3a) (480 mg, 0.688 mmol) with [NO]BF4 (166 mg, 1.42 mmol) in CH2Cl2 (30 mL) for 1 h at 40 °C afforded according to method D the product [Ru(bdpma)(O2CC(O)Me)(NO)(PPh3)]BF4 (14a) as a pale red powder.

Yield 468 mg (0.575 mmol, 84%). mp 125 °C (dec.). IR (CH2Cl2): ν = 1912 vs (NO), 1706 s (CO2−), 1653 m (CO2−), 1560 m (C≡N), 1483 w, 1465 v, 1437 m, 1419 vw cm−1. 1H NMR (CDCl3, 150 MHz): δ = 1.95, 2.36, 2.57, 2.62 (s, 12H, C3−CH3), 2.56, 2.62 (s, 3H, C5−CH3), 6.22, 6.24 (s, 2H, H4aram), 6.71 (s, 1H, CH), 7.30–7.70 (m, 18H, Ph and PPh3), 7.99 (vt, 2H, o-Phe). 13C NMR (CDCl3, 62.9 MHz): δ = 11.1, 11.5, 13.9, 14.3 (C3−CH3), 68.2 (CH1), 110.1 (d, C4 or C4′), 143.5 (C4 or C4′), 120.0 (d or C3−CH3), 131.5 (d, C5−CH3), 127.2 (d or C3−CH3), 168.1 (COOH). 31P NMR (CDCl3, 161.8 MHz): δ = 24.1. Anal. Calcd for C38H36BF6N6O3Ru: C, 53.0; H, 4.4; N, 6.8; O, 3.6. Found: C, 53.0; H, 4.6; N, 6.8; O, 3.6.

[Ru(bdpma)(O2CC(O)Et)(NO)(PPh3)]BF4 (14b). Reaction of [Ru(bdpma)(O2CC(O)Et)(PPh3)] (3b) (450 mg, 0.632 mmol) with [NO]BF4 (151 mg, 1.29 mmol) in CH2Cl2 (50 mL) for 1 h at 40 °C according to method D afforded the product [Ru(bdpma)(O2CC(O)Et)(NO)(PPh3)]BF4 (14b) as a pale red powder.

Yield 500 mg (0.603 mmol, 95%). mp 120 °C (dec.). IR (CH2Cl2): ν = 1911 vs (NO), 1670 s (CO2−), 1653 m (CO2−), 1561 m (C≡N), 1483 w, 1462 w, 1437 m, 1419 vw cm−1. IR (KBr): ν = 1904 vs (NO), 1701 vs (CO2−), 1649 s (CO2−), 1561 m (C≡N), 1484 w, 1462 w, 1439 m, 1421 vw 1416 vw cm−1. UV/Vis (CH2Cl2): λmax/nm (log ε) = 237.0 (4.37), 276.0 (4.31). FAB MS (NBOH): m/z (%) = 702 (100) [M* + H], 641 (52) [M* + O2C(O)Me], 363 (21) [M* − bdpma − O2C(O)Me − NO]. 1H NMR (CDCl3, 150 MHz): δ = 2.01 (s, 3H, C3−CH3), 2.24 (s, 3H, C−CH3), 2.31 (s, 3H, C(O)−CH3), 2.57 (s, 3H, C−CH3), 2.64 (s, 3H, C−CH3), 6.26 (s, 1H, H4aram), 6.32 (s, 1H, H4aram), 6.73 (s, 1H, CH), 7.38 (m, 6H, o-PPh3), 7.49 (m, 6H, m-PPh3), 7.64 (m, 3H, p-PPh3). 13C NMR (CDCl3, 150 MHz): δ = 11.1 (C−CH3), 11.5 (C−CH3), 13.5 (C−CH3), 14.2 (C−CH3), 27.6 (C(O)−CH3), 68.1 (CH1), 110.3 (d, C4, 1JCP = 3.0 Hz), 111.6 (C), 124.8 (d, 1JCP = 5.45 Hz), 129.7 (d, 1JPP = 11.4 Hz), 133.2 (p-PPh3), 133.5 (d, 1JPP = 9.8 Hz), 145.4 (d, 1JCP = 1.7 Hz), 147.0 (C), 154.2 (d, 1JCP = 2.1 Hz), 158.2 (C), 163.3 (COOH), 168.3 (C(O)−CO2−), 192.9 (C(O)). 31P NMR (CDCl3, 161.8 MHz): δ = 24.1. Anal. Calcd for C39H38BF6N6O3Ru: C, 52.4; H, 4.4; N, 6.8; O, 3.6. Found: C, 52.4; H, 4.6; N, 6.8; O, 3.6.

Table 1. Structure Determination Details of Compounds 4, 5a, 7a, and 8b

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<tr>
<th>Compound</th>
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<th>5a</th>
<th>5b</th>
<th>7a</th>
<th>8b</th>
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<td>P1 (2)</td>
<td>P1 (2)</td>
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<td>19.4466 (4)</td>
<td>17.8764 (7)</td>
<td>17.8764 (7)</td>
<td>17.390 (10)</td>
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<td>90</td>
<td>90</td>
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<td>90</td>
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<td>β [°]</td>
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<td>123 (2)</td>
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<td>6605</td>
<td>3327</td>
<td>6925</td>
<td>6925</td>
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<td>0.0361, 0.0694</td>
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<td>0.0933, 0.0782</td>
<td>0.0688, 0.1169</td>
<td>0.0688, 0.1169</td>
</tr>
</tbody>
</table>

3.1 Hz), 111.7 (C3), 124.8 (d, i-PPh3), 129.6 (54.4 Hz), 129.7 (d, m-PPh3), 133.2 (p, o-PPh3), 133.5 (d, o-PPh3), JCP = 9.8 Hz), 145.3 (d, C5, JCP = 1.9 Hz), 174.0 (C5), 154.2 (d, C5), JCP = 2.1 Hz), 158.2 (C5), 163.4 (CO2), 168.8 (CO2), 196.0 (C0). 13C NMR (CDCl3, 161.8 MHz): δ = 24.0. Anal. Calc. for C20H21BF22N2O3Ru: 42.5% C, 3.92% H, 5.0% N, 18.4% B, 11.9% F.

Calculations. All density-functional theory (DFT)-calculations were carried out by using the Jaguar 6.0015 software running on Linux 2.4.18-14smp on five Athlon MP 2800+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. X-ray structures or MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay–Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. Orbital plots were obtained using Maestro 7.0.113, the graphical interface of Jaguar. Rotational barriers have been calculated fully relaxed, fixing one torsion angle around the rotated bond, and optimizing all remaining degrees of freedom. Torsion angles were modified in steps of 5° beginning from the structure of minimum energy.

X-ray Structure Determinations. Single crystals of 4, 5a, 7a, 8b, 9b, 10b, and 14a were placed with Paratone-N or glue onto a glass fiber. A modified Siemens P4-Diffractometer and an Enraf Nonius CAD-4 Mach3 diffractometer were used for data collection (graphite monochromator, Mo Kα radiation, λ = 0.7073 Å, scan rate 4°–30° min⁻¹). The structures were solved by using either direct or Patterson methods (Siemens SHELXS-9310 and refined with full-matrix least-squares against F² [Siemens SHELXL-9710]). A weighting scheme was applied in the last steps of the refinement with w = 1/[σ(F²) + (aP)² + bP] and P = 2(F² + Max(F²,o)/3. The hydrogen atoms were included in calculated positions and refined in a “riding model”. In the asymmetric units of 8b and 14a one molecule of dichloromethane was co-crystallized per complex molecule, and so were two dichloromethane molecules in the complexes 4, 5a, and 10b. In case of complex 9b two chloroform molecules were found per asymmetric unit. All co-crystallized solvent molecules were included into the models and refined anisotropically. The PPh₃ as well as the 2-oxocarboxylato ligand exhibited a severe disorder in case of 8b. Thus, several restraints had to be applied, and the structure allows no detailed discussion of distances and angles. The structure pictures were prepared with the program Diamond 2.1e.11 All details and parameters of the measurements are summarized in Tables 1 and 2.

Results and Discussion

In a first attempt to exchange one PPh₃ for an acetonitrile ligand, the chlorido complex [Ru(bdmpz)Cl(PPh₃)] (1) was


heated under reflux in acetonitrile. Indeed, one PPh₃ ligand is released and the chiral acetonitrile complex [Ru(bdmpza)Cl(NCMe)(PPh₃)] ([9]) is formed when the PPh₃ is extracted with n-pentane, although this procedure has to be repeated several times to obtain a complete conversion (Scheme 1).

The complex 4 exhibits two sets of signals for the pyrazolyl donors in the ¹H and ¹³C NMR spectra. The acetonitrile signals have been assigned to 1.88 ppm in the ¹H NMR spectrum and to 3.67 and 124.0 ppm in the ¹³C NMR spectrum. Only one singlet for a single PPh₃ ligand is found in the ³¹P NMR spectrum at 48.8 ppm. The IR signal of the coordinated 2-oxocarboxylato ligands exhibits a purple color due to a MLCT transition. Acetonitrile solutions of 4 changed to yellow upon standing within some days, clearly indicating a change to κ¹¹-coordination and the formation of [Ru(bdmpza)(O₂CC(O)Me)(NCMe)(PPh₃)] (3b) in acetonitrile for 2 h. An analogous reaction with the 2-oxocarboxylato complexes [Ru(bdmpza)Cl(NCMe)(PPh₃)] (3c) under reflux with acetonitrile for 2 h. An analogous reaction with the 2-oxocarboxylato complexes [Ru(bdmpza)(O₂CC(O)Me)(NCMe)(PPh₃)] (3a) and [Ru(bdmpza)(O₂CC(O)Et)(PPh₃)] (3b) was not successful so far. On the other hand, we reacted the κ¹²O¹1,κ¹'O²-coordinated 2-oxocarboxylato complexes [Ru(bdmpza)(O₂CC(O)Me)(PPh₃)] (3a) and [Ru(bdmpza)(O₂CC(O)Et)(PPh₃)] (3b) with acetonitrile within 5 h to form the carboxylato complexes [Ru(bdmpza)(O₂CCMe₃)(NCMe)(PPh₃)] (5a) and [Ru(bdmpza)(O₂CPh)(NCMe)(PPh₃)] (5b) (Scheme 1).

The acetato complex 5a exhibits two sets of signals for the diastereotopic pyrazolyl groups in the ¹H and ¹³C NMR spectra. One signal at 2.22 ppm in the ¹H NMR spectrum and two signals at 4.60 and 124.7 ppm in the ¹³C NMR spectrum have been assigned to the acetonitrile ligand. The ³¹P NMR singlet of the PPh₃ ligand was observed at 53.4 ppm. X-ray structure determinations revealed the molecular structures of 4 and 5a which are depicted in Figures 1 and 2. Selected bond lengths and angles are reported in Table 4. The coordination geometry of these complexes is approximately octahedral, and the distances and angles in these two complexes are


![Figure 1. Molecular structure of [Ru(bdmpza)Cl(NCMe)(PPh₃)] (4) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.](image)

![Figure 2. Molecular structure of [Ru(bdmpza)(O₂CC(O)Me)(NCMe)(PPh₃)] (5a) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.](image)
relatively uniform. Because of the space groups \( P2_1/a \) and \( P1 \), both enantiomers of the chiral complexes 4 and 5a can be found in the unit cells. The distances and angles agree well with those of complex 1 which we reported on lately.\(^3\) It is interesting to note that the positions of the chlorido ligand and also the acetato ligand are trans to a pyrazol donor of the bdmpza ligand. In contrast, so far most molecular structures showed a chlorido ligand trans to the carboxylato donor of the bdmpza ligand. 3,4

The complex \([\text{Ru(bdmpz}a)(\text{O}_2\text{CPh})(\text{NCMe})(\text{PPh}_3)]\) (5b) does form two isomers which show a rather similar pattern in the NMR spectra. The acetonitrile signals have been assigned for both isomers (\(1^H \text{NMR}: 2.23 \) and 1.92 ppm; \(1^3C \text{NMR}: 2.23, 124.7, \) and 3.56, 124.1 ppm). The two signals in the \(3^1P \text{NMR} \) spectrum at 53.6 and 51.9 ppm are due to the \(\text{PPh}_3 \) ligands of the two isomers. So far, we could not deduce which of the three possible structural isomers are preferentially formed, but we assume one isomer might have a configuration similar to 5a and the other one a configuration with the benzoato ligand trans to the bdmpza carboxylato donor.

The \(\text{CO}_2^-\) signals in the \(1^3C \text{NMR} \) spectra of the acetato or benzoato ligand in 5a and 5b, respectively, have been shifted by 9 ppm to higher field compared to 2a and 2b, on account of the \(\kappa^1\text{O}^-\)-coordination of the acetato and benzoato ligand. The IR bands assigned to \(\nu(\text{CtN})\) of the acetonitrile ligands at 2271 (5a) and 2270 cm\(^{-1}\) (5b) are reasonable compared to other complexes such as those of the Tp complex \([\text{RuTpCl(NCMe)\text{PPh}_3]}\) (see Table 3). In the FAB mass spectra molecular mass peaks fit to \([\text{Ru(bdmpz}a)(\text{O}_2\text{CMe})(\text{NCMe})(\text{PPh}_3)]\) (5a) and \([\text{Ru(bdmpz}a)(\text{O}_2\text{CPh})(\text{NCMe})(\text{PPh}_3)]\) (5b), although the 100% peaks are assigned to \([\text{Ru(bdmpz}a)(\text{O}_2\text{CMe})(\text{PPh}_3)]\) (2a) and \([\text{Ru(bdmpz}a)(\text{O}_2\text{CPh})(\text{PPh}_3)]\) (2b).

Because of the problems that came about in these reactions of the acetonitrile sp-N donor with the carboxylato and 2-oxocarboxylato complexes, pyridine has been tested as sp\(^2\)-N donor ligand instead. A complete conversion within 3 days could be achieved to give complexes 7 and 8, respectively, for the carboxylato complexes 2a and 2b as well as for the 2-oxocarboxylato complexes 3a–3c (Scheme 2) by using 10 equiv of pyridine in dichloromethane.

A similar reaction with \([\text{Ru(bdmpz}a\text{Cl[PPh}_3]}\) (1) was also successful and afforded the complex \([\text{Ru(bdmpz}a\text{Cl[PPh}_3]}\) (6) as well as the complexes 7a–7c. All pyridine complexes 6, 7a, 7b, and 8a–8c exhibit \(1^H \) and \(1^3C \text{NMR} \) spectra typical for chiral complexes with two sets of pyrazolyl signals. The PPh\(_3\) singlets in the \(3^1P \text{NMR} \) spectrum appear around 50 ppm and are thus shifted by 10 ppm to higher field compared to the educt complexes. Mass peaks in the FAB mass spectra affirm the composition of the complexes.

The \(1^3C \text{NMR} \) \(\text{CO}_2^-\) signals of the \(\kappa^1\text{O}^-\)-coordinated carboxylato ligands are shifted by 11 ppm to higher field compared to the \(\kappa^2\text{carboxylato complexes (178.0 (7a) and 171.1 ppm (7b)). The ketocarbonyl signals of the 2-oxocarboxylato complexes exhibit a similar 15 ppm shift to higher}

<table>
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<th>complex</th>
<th>IR (C=\text{N}) [cm(^{-1})]</th>
<th>(1^H ) (MeCN) [ppm]</th>
<th>(1^3C ) (MeCN) [ppm]</th>
<th>(3^1P) [ppm]</th>
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<tr>
<td>([\text{Ru(bdmpz}a\text{Cl}[\text{NCMe}][\text{PPh}_3]})) (4)</td>
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<td>1.88</td>
<td>3.67</td>
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<td>2.23; 124.7</td>
<td>53.6</td>
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<tr>
<td>([\text{Ru(bdmpz}a\text{(O}_2\text{CC(O)}\text{Ph)}\text{(NCMe)}[\text{PPh}_3]})) (3c × NCMe)</td>
<td>2278(^a)</td>
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<td>3.8</td>
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</tr>
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<td>2258(^b)</td>
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</table>

\(^a\) CH\(_2\)Cl\(_2\). \(^b\) KBr. \(^c\) Diffuse reflectance.
field and are assigned to 197.6 (8a), 200.3 (8b), and 190.4 ppm (8c), respectively. These are typical values of noncoordinated keto ligands.3b

Crystals suitable for a single crystal X-ray structure determination have been obtained of [Ru(bdmpza)(O2CMe)(PPh3)(py)] (7a) and [Ru(bdmpza)(O2CC(O)Et)(PPh3)(py)] (8b) (Figure 3 and 4; Table 5). The pyridine and the PPh3 coordinate trans to the pyrazolyl groups. The acetato and the 2-oxocarboxylato ligands are disordered. Only one of the two alternative orientations that have been included into the structure model is shown here for clarity.

Figure 3. Molecular structure of [Ru(bdmpza)(O2CMe)(PPh3)(py)] (7a) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Figure 4. Molecular structure of [Ru(bdmpza)(O2CC(O)Et)(PPh3)(py)] (8b) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. PPh3 and O2CC(O)CH2CH2 ligands are disordered. Only one of the two alternative orientations that have been included into the structure model is shown here for clarity.

Figure 5. Contour plots (Kohn–Sham orbitals) of (a) the HOMO-2 of pyridine, (b) the HOMO of pyridine, and (c) the LUMO of pyridine.

Although the π-acceptor properties of pyridine are generally accepted to be moderate,16 the aromatic system of this ligand allows back-bonding as pointed out by the contour plots of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO, Figure 5b and 5c). For a discussion of the almost identical orientation of the pyridine ligands in 7a and 8b DFT calculations were performed with the 16 valence electron fragment [Ru(bdmpza)(O2CPh)(PPh3)]. Figure 6 shows contour plots of its LUMO, HOMO, HOMO-1, and HOMO-2.

According to these plots, especially the HOMO-2 of the 16 valence electron fragment seems to determine the orientation of the pyridine ligands in the complexes [Ru(bdmpza)-(O2CMe)(PPh3)(py)] (7a) and [Ru(bdmpza)(O2CC(O)Et)(PPh3)(py)] (8b). The pyridine ligands in 7a and 8b are almost in a plane with O(1)−Ru−OAc-Npy or O(1)−Ru−O2oxocarb-Npy, respectively (Figure 7a and 7b). This orientation allows a Ruπ=Npy back-donation by interaction of the pyridine π* orbital with the HOMO-2.

Nevertheless, the pyridine ligands in 7a and 8b are slightly tilted out of the Ocarboxylate−Ru−Npy planes as indicated by the absolute values of the torsion angles [7a, |∠(OAc−Ru−Npy−Cpy)| = 22.2(2)°; 8b, |∠(O2oxocarb−Ru−Npy−Cpy)| = 17.9(3)°] (Figure 7). This agrees well with the calculated (DFT) structure of minimum energy (∠(OAc−Ru−Npy−Cpy) = 17.7°) for complex 7a. To investigate this deviation from the ideal perpendicular orientation by some 20°, the rotational barrier of the pyridine ligand in [Ru(bdmpza)(O2CMe)(PPh3)(py)] (7a) has been calculated in steps of 5° beginning from the minimum energy structure (Figure 8). A rotation of the pyridine ligand by 20° causes a rather small increase in energy by 3 to 5 kJ/mol. Thus, this deviation might be due to crystal-packing effects or interactions of the pyridine with PPh3 or the pyrazolyl Me3. Rather similar findings have been reported recently by us for a vinylidene ligand instead of pyridine in an analogous complex [Ru(bdmpza)Cl(=C=CH2)Cl(PPh3)].4

ruthenium vinylidene complexes \([\text{Ru(bdmpz)(=C=CHR)}(\text{PPh}_3)]\), as mentioned above, we already obtained a carbyl complex \([\text{Ru(bdmpz)}\text{Cl}(\text{CO})(\text{PPh}_3)]\) by a degradation reaction.\(^4\) \([\text{Ru(bdmpz)}\text{Cl}(\text{CO})(\text{PPh}_3)]\) can also be obtained by replacing a \text{PPh}_3 ligand of \([\text{Ru(bdmpz)}\text{Cl}(\text{PPh}_3)_2]\) (1) with \text{CO}.\(^4\) Therefore, we decided to expose the carboxylato complexes \([\text{Ru(bdmpz)}(\text{O}_2\text{CMe})(\text{PPh}_3)]\) (2a) and \([\text{Ru(bdmpz)}(\text{O}_2\text{CPh})(\text{PPh}_3)]\) (2b) to \text{CO}. Flushing solutions of 2a and 2b with \text{CO} gas resulted within 2 h in a complete conversion of these complexes to the carbyl complexes \([\text{Ru(bdmpz)}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)]\) (9a) and \([\text{Ru(bdmpz)}(\text{O}_2\text{CPh})(\text{CO})(\text{PPh}_3)]\) (9b) (Scheme 3).

Mass spectroscopic data with \([\text{M}^+]\) peaks at \(m/z\) 698 (9a) and 760 (9b) revealed the formation of the carbyl complexes 9a and 9b.}

**Figure 6.** Contour plots (frontier Kohn–Sham orbitals) of the \([\text{Ru(bdmpz)}(\kappa^1-\text{O}_2\text{CPh})(\text{PPh}_3)]\) 16VE fragment (DFT-calculations) with (a) LUMO, (b) HOMO, (c) HOMO-1, and (d) HOMO-2.

**Figure 7.** Orientation of the pyridine ligand in (a) \([\text{Ru(bdmpz)}(\text{O}_2\text{CMe})(\text{PPh}_3)(\text{py})]\) (7a) and (b) in \([\text{Ru(bdmpz)}(\text{O}_2\text{CC(O)Et})(\text{PPh}_3)(\text{py})]\) (8b).

Ruthenium Carboxylato and 2-Oxocarboxylato Complexes

Because of the chiral $C_1$ geometry of the complexes, again two sets of signals are observed in the $^1H$ and $^{13}C$ NMR spectra for the diastereotopic pyrazolyl groups. The $^{13}C$ NMR carboxylate signals of the $\kappa^1O$-coordinated acetato and benzoato ligands are shifted by 11 ppm to higher field (173.3 ppm (9a), 172.6 ppm (9b)) compared to the complexes 2a and 2b with $\kappa^2O,O'$-coordinated carboxylate ligands. Two additional bands at 1624 cm$^{-1}$ (9a) and 1636 cm$^{-1}$ (9b) belong to the carboxylate vibrations $\nu_{\text{sym}}(\text{CO}_2^{-})$ of the $\kappa^1O$-coordinated acetato and benzoato ligands. The $^{31}P$ NMR singlets of the PPh$_3$ ligands at 43.3 (9a) and 43.6 ppm (9b) are almost identical to the singlet we reported recently for [Ru(bdmpza)Cl(CO)(PPh$_3$)] (41.7 ppm). IR signals at 1977 (9a) and 1978 (9b) cm$^{-1}$ (CH$_2$Cl$_2$) and doublets in the $^{13}C$($^1H$) NMR spectra at 205.3 ppm ($^2J_{CP}$ = 19.8 Hz) and 204.2 ppm ($^2J_{CP}$ = 21.2 Hz) can be assigned to the carboxyl ligands and agree also with the data observed for [Ru(bdmpza)Cl(CO)(PPh$_3$)].$^4$ Several carbonyl ruthenium complexes bearing Tp (BH(pz)$_3$), Cp ($\eta^5$-C$_5$H$_5$), and Cp* ($\eta^5$-C$_5$Me$_5$) ligands are described in the literature (see Table 6).$^{17-23}$

This allows a closer discussion of the electron donating properties of the bdmpza ligand. The carbonyl vibrations are observed at higher wavenumbers compared to analogous Cp*, Cp, and Tp ruthenium complexes such as [RuCl(CO)(PPh$_3$)] (1958 cm$^{-1}$), $[\text{RuCl}(\text{O}2\text{CMe})(\text{CO})(\text{PPh}_3)]$ (1925 cm$^{-1}$), or [RuCl(CO)(PPh$_3$)] (1965 cm$^{-1}$) (Table 4). This implies a weaker $\text{Ru}_{\text{L}}^1\text{C}_{\text{P}}^2$ back-donation into the carbonyl ligand of the bdmpza complexes. Thus, in these ruthenium complexes the bdmpza ligand seems to be less electron donating compared to Cp*, Cp, and even Tp ligands. Crystals of [Ru(bdmpza)(O$_2$CPh)(CO)(PPh$_3$)] (9b) suitable for an X-ray structure determination have been obtained from a CHCl$_3$ solution. The molecular structure (Figure 9, Table 7) reveals the formation of a carboxyl complex and the $\kappa^1O$-coordination of the benzoate ligand $\text{trans}$ to the bdmpza carboxylate donor.

The Ru–C(3) and C(3)–O(3) bond distances of the carboxyl ligand in 9b at 1.870(5) Å and 1.145(6) Å are in the expected range of other ruthenium carboxyl complexes (see Table 6).$^{17-20}$ These Cp and Tp ruthenium carboxyl complexes show molecular structures with $d$(Ru–CO) = 1.872(6), $d$(C–O) = 1.132(8) Å for [RuCl(PPh$_3$)(CO)] and $d$(Ru–CO) = 1.848(6), $d$(C–O) = 1.137(8) Å for [RuCl(PPh$_3$)] (see Table 6). Also, the bond distances of the previously reported complex [Ru(bdmpza)Cl(CO)(PPh$_3$)] (d(Ru–CO) = 1.821(5) Å, d(C–O) = 1.151(6) Å) are in this range.$^4$ The angle Ru–C(3)–O(3) is almost linear (177.0(4)°). The distance $d$(Ru–N11) = 2.183(3) Å is significantly longer compared to $d$(Ru–N21) = 2.148(4) Å, indicating the $\text{trans}$ influence of the carbonyl ligand.

Whereas CO is able to replace one $O$-donor of a hemilabile chelating $\kappa^2O,\kappa^1O$-carboxylato ligand, an analogous reaction with $\kappa^2O,\kappa^1O^2$-oxocarboxylato complexes has not been successful so far. Solutions of [Ru(bdmpza)(O$_2$CC(O)Me)(PPh$_3$)] (3a) and [Ru(bdmpza)(O$_2$CC(O)Ph)(PPh$_3$)] (3e) flushed with CO showed only traces of newly formed products beside the educts in the NMR spectra. Thus, 2-oxocarboxylato ligands seem to be tighter bound ligands compared to the carboxylato ligands.

Besides CO, gaseous SO$_2$ can act as a good $\sigma$-donor and $\pi$-acceptor ligand too. Various coordination modes to metals are known for SO$_2$ ligands. A $\eta^1$-coordination via the sulfur atom is possible with a planar or a pyramidal geometry. Also a $\eta^2$-coordination of SO$_2$ via a sulfur and an oxygen atom can take place (see Figure 10).$^{24-27}$

Furthermore, SO$_2$ can be coordinated via the oxygen atom and might also act as a bridging ligand.$^{25-27}$ Only a few mainly cationic ruthenium SO$_2$ complexes such as [RuCl(chir)-SO$_2$]PF$_6$ and [RuCl($^6$S$^4$S)SO$_2$]Cl have so far been described in the literature.$^{7b,28-30}$ Thus, we also investigated the reactivity of carboxylato and 2-oxocarboxylato complexes toward SO$_2$. Solutions of [Ru(bdmpza)(O$_2$CMe)(PPh$_3$)] (2a) and [Ru(bdmpza)(O$_2$CPh)(PPh$_3$)] (2c) in CH$_2$Cl$_2$ were flushed with gaseous SO$_2$ for 30 min to obtain the SO$_2$ complexes [Ru(bdmpza)-(O$_2$CMe)(PPh$_3$)(SO$_2$)] (10a) and [Ru(bdmpza)(O$_2$CPh)(PPh$_3$)(SO$_2$)] (10b) in high yields (Scheme 3). The IR spectra exhibit two new bands at 1284 and 1128 cm$^{-1}$ (for 10a) and 1286 and 1129 cm$^{-1}$ (for 10b). These have been assigned to the

asymmetric and symmetric SO₂ vibrations. Such values are typical for SO₂ complexes with a \( \eta^1 \)-planar geometry, which usually reveal two bands in between 1300 to 1225 cm\(^{-1} \) and 1140 to 1060 cm\(^{-1} \).\(^\text{24,25} \) These vibrations of the bdmpza ruthenium SO₂ complexes are found at smaller wavenumbers compared to the cyclopentadienyl complex \([\text{Ru(Cp)}(\text{PPh}_3)_2(\text{SO}_2)]\text{Cl}\) (1294 and 1118 cm\(^{-1} \))\(^\text{28} \) but at higher wavenumbers compared to the Cp* ruthenium complex \([\text{RuCp}^* (\text{PPh}_3)_2(\text{SO}_2)]\text{Cl}\) (1277 and 1110 cm\(^{-1} \))\(^\text{28} \) (see Table 8). The coordination of the SO₂ ligand is also backed by an M⁺ peak in the FAB mass spectrum.

The unsymmetrical C₁ geometry of both SO₂ complexes 10a and 10b is clearly indicated by two sets of signals in the \(^1\)H and \(^{13}\)C NMR spectra, which have been assigned to the two pyrazolyl donors. The \(^{13}\)C NMR signal of the \( \kappa^1 \text{O}^{-} \)-coordinated carboxylato donor is shifted by 9 ppm to higher field compared to the \( \kappa^2 \text{O}^{-},\text{O}^{\prime} \)-coordinated carboxylato complexes 2a and 2b. This shift and the \(^{31}\)P NMR signals of the PPh₃ ligand at 45.4 and 44.6 ppm agree well with the carbonyl complex data discussed above. Similar to the CO ligand, SO₂ is able to replace one O⁻-donor of the hemilabile, chelating \( \kappa^2\text{O}^{-},\text{O}^{\prime} \)-carboxylato ligand. Again, a similar reaction of SO₂ with the 2-oxocarboxylato complexes \([\text{Ru(bdmpza)}(\text{O}2\text{CPh})(\text{CO})(\text{PPh}_3)]\) (3a), \([\text{Ru(bdmpza)}(\text{O}2\text{C(CH₃)})(\text{PPh}_3)]\) (3b), and \([\text{Ru(bdmpza)}(\text{O}2\text{CC}(\text{O})\text{Ph})(\text{PPh}_3)]\) (3c) has not been successful so far. An X-ray structure determination of \([\text{Ru(bdmpza)}(\text{O}2\text{CPh})(\text{PPh}_3)(\text{SO}_2)]\) (10b) shows a molecular structure with the SO₂-ligand \( \text{trans} \) to a pyrazolyl donor of the bdmpza ligand (Figure 11, Table 9). This position is also preferred by the other acceptor ligands, such as CO and pyridine (Figures 3, 4, and 10). The bond distances from the bdmpza and PPh₃ ligands to the ruthenium and also the angles between the coordinated

\[\text{Scheme 3. Syntheses of Carbonyl and SO}_2\text{ Complexes}\]

\[\text{Figure 9. Molecular structure of } [\text{Ru(bdmpza)}(\text{O}2\text{CPh})(\text{CO})(\text{PPh}_3)](9b) \text{ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.}\]

\[\text{Table 4. Selected Bond Lengths [Å] and Angles [deg] of Complexes 4 and 5a}\]

\[\begin{array}{cccccc}
\text{Bond} & \text{Distance [Å]} & \text{Angle [deg]} & \text{Bond} & \text{Distance [Å]} & \text{Angle [deg]} \\
\text{Ru–N(11)} & 2.106(3) & & \text{Ru–P} & 2.301(10) & \\
\text{Ru–N(21)} & 2.135(3) & & \text{Ru–N(71)} & 1.993(3) & \\
\text{Ru–O(1)} & 2.098(2) & & \text{N(71)–C(71)} & 1.138(4) & \\
\text{Ru–Cl} & 2.4282(9) & & \text{C(71)–C(72)} & 1.454(5) & \\
\text{Ru–O(61)} & 2.075(4) & & & & \\
\text{N(11)–Ru–N(21)} & 83.20(11) & & \text{O(1)–Ru–N(71)} & 177.88(11) & \\
\text{O(1)–Ru–N(11)} & 86.27(10) & & \text{P(1)–Ru–Cl} & 86.60(3) & \\
\text{O(1)–Ru–N(21)} & 87.12(10) & & \text{P(1)–Ru–O(61)} & 90.71(13) & \\
\text{O(1)–Ru–P} & 90.30(7) & & \text{N(11)–Ru–Cl} & 171.55(8) & \\
\text{N(21)–Ru–P} & 174.60(8) & & \text{N(11)–Ru–(O61)} & 168.03(16) & \\
\text{P–Ru–N(71)} & 91.69(9) & & \text{Ru–N(71)–C(71)} & 174.7(3) & \\
\end{array}\]

\[\text{Table 5. Selected Bond Lengths [Å] and Angles [deg] of the Complexes 7a and 8b}\]

\[\begin{array}{cccccc}
\text{Bond} & \text{Distance [Å]} & \text{Angle [deg]} & \text{Bond} & \text{Distance [Å]} & \text{Angle [deg]} \\
\text{Ru–N(11)} & 2.138(3) & & \text{N(11)–Ru–N(21)} & 85.71(13) & \\
\text{Ru–N(21)} & 2.096(3) & & \text{O(1)–Ru–N(11)} & 85.27(11) & \\
\text{Ru–O(1)} & 2.110(3) & & \text{O(1)–Ru–N(21)} & 87.39(11) & \\
\text{Ru–N(1)} & 2.080(3) & & \text{O(1)–Ru–O(3)} & 177.31(11) & \\
\text{Ru–P} & 2.090(3) & & \text{O(1)–Ru–O(3)} & 171.02(9) & \\
\text{Ru–P} & 2.305(12) & & \text{N(11)–Ru–P} & 172.83(13) & \\
\text{C–O(3)} & 1.286(5) & & \text{N(21)–Ru–N(1)} & 173.03(11) & \\
\text{C–O(4)} & 1.221(5) & & \text{N(21)–Ru–N(1)} & 173.03(11) & \\
\end{array}\]

\[\text{Note: \( \kappa^1 \) and \( \kappa^2 \) refer to the coordination mode of the carboxylato ligand.}\]

ligands are more or less the same compared to the molecular structures of $2a \times \text{H}_2\text{O}$ and $3c$.

The $\eta^1$-benzoato bond lengths of $10b$ [$d(\text{C}(3)−\text{O}(5)) = 1.271(8)$ Å; $d(\text{C}(3)−\text{O}(6)) = 1.272(8)$ Å] are almost equal. Thus, both oxygen donors seem to share the negative charge of the benzoato ligand. The phenyl group of the benzoato ligand in the SO$_2$-complex $10b$ deviates by $−21.1(10)^\circ$ from the RCO$_2$-plane. A similar twist by $26.4(6)^\circ$ is observed for the carbonyl complex $9b$. The $\eta^1$-bound SO$_2$ is not planar but distorted with a distance of 0.685(11) Å between ruthenium and the O(3)−S(1)−O(4) plane. The bond distances S(1)−O(3) [1.452(5) Å] and S(1)−O(4) [1.456(5) Å] agree well with those of other ruthenium SO$_2$ complexes such as [RuCl(CO)(PPh$_3$)]$_2$PF$_6$ [1.432(6) and 1.458(6) Å] (see Table 8). The Ru−S(1) distance [2.182(2) Å] is significantly longer than those found in other ruthenium SO$_2$ complexes like [RuCl(chir)SO$_2$]PF$_6$ [2.128(2) Å] or trans-[Ru(O$_2$CCF$_3$)$_2$(NH$_3$)$_2$(SO$_2$)]$_2$[O$_2$CCF$_3$]) [2.0945(5) Å].$^{26,31}$

The S(1)−O(6) distance between the SO$_2$ and the benzoato ligand is surprisingly short [2.022(5) Å]. In fact, it lies in

$\eta^1$-pyramidal ligands.

Figure 10. Coordination modes of SO$_2$ in transition metal complexes.$^{21−26}$

Table 6. Spectroscopic and Structure Data of Various Ruthenium Carbonyl Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>IR (CO) $^{[\text{cm}^{-1}]}$</th>
<th>$d$(Ru−CO)/$d$(C−O) $^{[\text{Å}]}$</th>
<th>$\angle$(Ru−C−O) $^{[\text{deg}]}$</th>
<th>$^{31}\text{P}$ $^{[\text{ppm}]}$</th>
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<tbody>
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<td>[Ru(bdmpza)(O$_2$CMe)(CO)(PPh$_3$)]$^2$</td>
<td>1977$^a$</td>
<td>1.870(5)</td>
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<td>[Ru(bdmpza)(O$_2$CPh)(CO)(PPh$_3$)]$^2$</td>
<td>1998$^b$</td>
<td>1.821(5)</td>
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<td>[RuTPCl(CO)(PPh$_3$)]$^2$</td>
<td>1958$^b$</td>
<td>1.911(20)</td>
<td>176.9(1.2)</td>
<td>48.9</td>
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<tr>
<td>[RuCl(CO)(PPh$_3$)]$^2$</td>
<td>1959$^b$</td>
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<td>178.3(8)</td>
<td>48.9</td>
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<td>53.9</td>
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*a* CH$_2$Cl$_2$, *b* KBr, *c* Nujol.

Table 7. Selected Bond Lengths [Å], Angles [deg], and Torsion Angles [deg] of Complex $9b$

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<th>Angle [deg]</th>
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<td>Ru−N(1)</td>
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<td>Ru−O(1)</td>
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<td>Ru−P</td>
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<td>Ru−O(3)</td>
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<td>Ru−C(3)</td>
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<td>N(11)−Ru−N(21)</td>
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Figure 11. Molecular structure of [Ru(bdmpza)(O$_2$CPh)(PPh$_3$)(SO$_2$)]$^{10b}$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

between the sum of the van der Waals radii (3.25 Å)$^{32}$ and a single S−O bond (around 1.6 Å) such as the S-OH bond in the complex [Ru(SO$_3$H)$_2$(bpy)$_2$] (1.586(5) and 1.612(8) Å).$^{33}$ This rather short distance indicates an intramolecular Lewis acid–base interaction between the Lewis acid SO$_2$ and the uncoordinated carboxylate oxygen. Because of the partial charge at this atom, this oxygen donor should be a rather good Lewis base.

In $\eta^1$-planar complexes SO$_2$ usually binds via the sulfur lone electron pair as a σ-donor to the metal. The LUMO of SO$_2$ which exhibits a * antibonding character, allows that bonding electron pair is formally provided by the filled metal d orbitals (Figure 6, Figure 12 and 13).$^{26}$ A $\eta^1$-pyramidal coordination of SO$_2$ ligands is observed for electron rich transition metal fragment such as Vaskas SO$_2$ complex [IrCl(CO)(PPh$_3$)$_2$(SO$_2$)].$^{26}$ In these $\eta^1$-pyramidal SO$_2$ complexes the bonding electron pair is formally provided by the electron-rich transition metal fragment (Figure 12).$^{26}$

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energy. Obviously, according to the angles around the SO$_2$ might be caused if either the LUMO of SO$_2$ is occupied and both are of similar angles [deg]

14a

$\angle$ (Ru-S=O)/$\angle$(O-S=O) [deg]

10b

$\triangleq$P [ppm]

Table 8. Spectroscopic and Structural Data Of Cp, Cp*, and bdmpza SO$_2$ Complexes

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<th>$\angle$(Ru-S=O)/$\angle$(O-S=O) [deg]</th>
<th>$\triangleq$P [ppm]</th>
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<td>1286$^a$</td>
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<tr>
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<td>1125$^b$</td>
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<td>[RuCp(chir)(SO$_2$)]PF$_6$$^{1b}$</td>
<td>1296$^c$</td>
<td>1.452(5)</td>
<td>114.2(3)</td>
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<td>[RuCp(chir)(SO$_2$)]Cl$_2$$^{1c}$</td>
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<td>1.456(5)</td>
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<td>$\triangleq$CH$_2$Cl, $^b$KBr, $^c$Nujol</td>
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Table 9. Selected Bond Lengths [Å] and Angles [deg] of Complex 10b

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<th>bond</th>
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<td>Ru--N(1)</td>
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<td>1.452(5)</td>
</tr>
<tr>
<td>Ru--N(21)</td>
<td>2.206(6)</td>
<td>1.456(6)</td>
</tr>
<tr>
<td>Ru--O(1)</td>
<td>2.092(4)</td>
<td>2.022(5)</td>
</tr>
<tr>
<td>Ru--P</td>
<td>2.331(2)</td>
<td>2.171(8)</td>
</tr>
<tr>
<td>Ru--S</td>
<td>2.182(2)</td>
<td>2.172(8)</td>
</tr>
<tr>
<td>Ru--O(S)</td>
<td>2.073(4)</td>
<td>0.685(11)</td>
</tr>
<tr>
<td>N(11)--Ru--N(21)</td>
<td>79.7(2)</td>
<td>120.8(2)</td>
</tr>
<tr>
<td>O(1)--Ru--N(21)</td>
<td>88.82(19)</td>
<td>118.1(2)</td>
</tr>
<tr>
<td>O(1)--Ru--N(21)</td>
<td>86.7(2)</td>
<td>114.2(3)</td>
</tr>
<tr>
<td>O(1)--Ru--P(1)</td>
<td>89.25(14)</td>
<td>356.3(7)</td>
</tr>
<tr>
<td>P(1)--Ru--S(1)</td>
<td>91.29(7)</td>
<td>21.1(10)</td>
</tr>
<tr>
<td>S(1)--Ru--O(1)</td>
<td>93.90(13)</td>
<td>0.685(11)</td>
</tr>
</tbody>
</table>

Table 10. Selected Bond Lengths [Å], Angles [deg], and Torsion Angles [deg] of the Complex 14a

<table>
<thead>
<tr>
<th>bond</th>
<th>length [Å]</th>
<th>angle [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru--N(11)</td>
<td>2.117(4)</td>
<td>1.562(6)</td>
</tr>
<tr>
<td>Ru--N(21)</td>
<td>2.130(3)</td>
<td>1.308(5)</td>
</tr>
<tr>
<td>Ru--O(1)</td>
<td>2.065(3)</td>
<td>1.205(6)</td>
</tr>
<tr>
<td>Ru--P</td>
<td>2.4174(15)</td>
<td>2.295(9)</td>
</tr>
<tr>
<td>Ru--O(41)</td>
<td>2.0283(14)</td>
<td>2.125(5)</td>
</tr>
<tr>
<td>Ru--N(31)</td>
<td>1.760(4)</td>
<td>1.587(7)</td>
</tr>
<tr>
<td>N(31)--O(31)</td>
<td>1.145(4)</td>
<td>1.211(6)</td>
</tr>
<tr>
<td>N(11)--Ru--N(21)</td>
<td>83.12(14)</td>
<td>95.78(11)</td>
</tr>
<tr>
<td>O(1)--Ru--N(21)</td>
<td>85.34(14)</td>
<td>175.26(11)</td>
</tr>
<tr>
<td>O(1)--Ru--N(21)</td>
<td>86.66(14)</td>
<td>94.34(16)</td>
</tr>
<tr>
<td>O(1)--Ru--P(1)</td>
<td>88.66(9)</td>
<td>97.34(16)</td>
</tr>
<tr>
<td>N(21)--Ru--O(41)</td>
<td>91.99(14)</td>
<td>93.20(16)</td>
</tr>
<tr>
<td>N(11)--Ru--O(31)</td>
<td>177.14(15)</td>
<td>169.39(11)</td>
</tr>
<tr>
<td>N(11)--Ru--O(41)</td>
<td>84.05(14)</td>
<td>177.44(11)</td>
</tr>
</tbody>
</table>

A transition from $\eta^1$-planar to $\eta^1$-pyramidal geometry might be caused if either the $\sigma^*$ orbital of the M-S bond or the LUMO of SO$_2$ is occupied and both are of similar angles. $^{26}$ Obviously, according to the angles around the SO$_2$ ligand [$\angle$Ru--S(1)--O(3) = 124.0(2$^c$), $\angle$Ru--S(1)--O(4) = 118.1(2$^c$), and $\angle$O(3)--S(1)--O(4) = 114.2(3$^c$)], the complex [Ru(bdmpza)(O$_2$CPh)(PPh$_3$)(SO$_2$)] (10b) is an almost $\eta^1$-planar complex in which SO$_2$ acts as $\sigma$-donor and $\pi$-acceptor. Because of the Lewis acid--base interaction between the coordinated SO$_2$ and the carboxylato ligand, indicated by the short S(1)--O(6) distance [2.022(5) Å], the SO$_2$ LUMO might be partially occupied. This could explain the slight deviation from the $\eta^1$-planar geometry, as well as the rather long Ru--S(1) distance. Until now, in the literature two SO$_2$ complexes with carboxylato ligands have been described: the mononuclear complex [Ru(O$_2$CCF$_3$)(NH$_3$)$_4$(SO$_2$)](O$_2$CCF$_3$)$_3$, in which SO$_2$ coordinates to the carboxylato ligand, and the dinuclear complex [Mo$_2$(O$_2$CCF$_3$)(NH$_3$)$_4$(SO$_2$)](O$_2$CCF$_3$)$_3$, which bridges SO$_2$ and carboxylato ligands. $^{31,34}$ Thus, to the best of our knowledge, 10a and 10b are the first examples of intramolecular Lewis acid--base adducts regarding SO$_2$ complexes.

Inspired by the reactivity of the carboxylato complexes toward CO and also by other ruthenium nitrosyl complexes described in the literature, such as [RuCpCl(NO)(PPh$_3$)]-PF$_6$$^{25}$ and complex [Ru(bdmpza)(O$_2$CC(O)Ph)(PPh$_3$)] (3c) was reacted with gaseous nitric oxide (NO). A significant color change from dark purple to blue was observed. Once the solvent and the excess of NO were removed in vacuo, a red product was obtained. The IR spectrum of CH$_2$Cl$_2$ shows two signals at 1698 and 1645 cm$^{-1}$ which have been assigned to asymmetric carboxylate vibrations of the bis(3,5-dimethylypyrazol-1-yl)acetate and the benzoylformato ligand. A vibration at 1911 cm$^{-1}$ indicates a linear nitrosyl ligand. $^{36}$ The $^1$H and $^{13}$C NMR spectra of the diamagnetic complex show two sets of methyl signals for the pyrazoles ($^1$H: 1.95, 2.36, 2.57, and 2.62 ppm; $^{13}$C: 11.1, 11.5, 13.9, and 14.3 ppm) as to be expected for an asymmetric geometry of the complex. The $^{13}$C NMR signal of the benzoylformate keto group is shifted slightly to higher field (202.8 → 186.7 ppm) compared to that of the educt complex 3c. This finding is rather similar to the pyridine complex 8c and consequently indicates an uncoordinated keto group. $^{13}$C NMR signals at 163.0 and 169.4 ppm were assigned to the $\kappa^1$-coordinated


carboxylato groups of the bdmpza and BF ligands. The 31P NMR singlet signal of the PPh3 ligand can be observed at 23.8 ppm. The product of the reaction can be precipitated from dichloromethane by adding diethylether. A molecular mass peak (FAB) at 791 agrees well with a complex cation \([\text{Ru(bdmpza)}(O2CC(O)Ph)(NO)(PPh3)]^+\) and thus with a coordinated nitrosonium (NO\(^+\)) ligand. Obviously, reaction of 3c with a large excess of gaseous NO results in the formation of a complex cation \([\text{Ru(bdmpza)}(O2CC(O)Ph)(NO)(PPh3)]^+\) (12) (Scheme 4).

One explanation\(^{37}\) for this NO\(^+\) formation might be the presence of NO2 in the reaction mixture, which is almost impossible to prevent in such reactions. Because NO of low purity grade has been used in our reaction, the presence of NO2 traces is very likely here. It is well-known that this might be a source of NO\(^+\) and NO3\(^-\).37 Thus, the counteranion might be nitrate NO3\(^-\), although nitrite NO2\(^-\) cannot be ruled out completely. Indeed analytical test reactions performed with 12 indicated traces of NO3\(^-\) but no NO2\(^-\). Unfortunately, so far we cannot prove the formation of a NO3\(^-\) counteranion unequivocally.

A similar reaction with an excess of NO is also possible with the acetato complex \([\text{Ru(bdmpza)}(O2CMe)(PPh3)]^+\) (2a), although no complete conversion could be achieved so far. Nevertheless, we were able to analyze the reaction product \([\text{Ru(bdmpza)}(O2CMe)(NO)(PPh3)]^+\) (11). \(^1\)H NMR signals at 1.94, 2.07, 2.25, 2.56, and 2.63 ppm have been assigned to the five methyl groups, and singlets at 6.20, 6.41, and 6.67 ppm belong to the pyrazolyl protons and the CH bridge, thus indicating again an unsymmetrical complex. Similar to the benzoylformato complex 12, the NO vibration is observed at 1911 cm\(^{-1}\) in the IR spectrum. The M\(^+\) peak at 700 in the FAB mass spectrum fits to a \([\text{Ru(bdmpza)}(O2CMe)(NO)(PPh3)]^+\) cation. Again, the nature of the anion, most likely nitrate NO3\(^-\), stays unresolved so far.

To verify the nitrosyl complex cations \([\text{Ru(bdmpza)}(O2CMe)(NO)(PPh3)]^+\) (11) and \([\text{Ru(bdmpza)}(O2CC(O)Ph)(NO)(PPh3)]^+\) (12) (Scheme 4).
The NO IR signals of the 2-oxocarboxylato complexes are faster compared to those of the carboxylato complexes. The diamagnetic property observed for the nitrosyl complexes indicates a high field shift of almost 25 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts.

The NO IR signals of the 2-oxocarboxylato complexes are faster compared to those of the carboxylato complexes. The diamagnetic property observed for the nitrosyl complexes indicates a high field shift of almost 25 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts.

In general, the yield of these reactions is rather high (84–98%). Reactions with the carboxylato complexes are faster compared to those of the carboxylato complexes. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts. The diamagnetic property observed for the nitrosyl complexes indicates a high field shift of almost 25 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts. The NO IR signals of the 2-oxocarboxylato complexes are shifted to higher field by 15 ppm compared to the educts.

The torsion angle $\angle(O(41)-C(41)-C(42)-O(43))$ of the 2-oxocarboxylato ligand in 14a ($-18.5(7)^\circ$) is bigger than in the benzoylformato complex 3c [$-0.3(5)^\circ$], but a conjugation across the $\pi$ system of the 2-oxocarboxylato ligand should still be possible. The bond distances of the nitrosyl ligand are $d(Ru-NO) = 1.760(4)$ Å and $d(N-O) = 1.145(4)$ Å in 14a, and the nitrosyl ligand is close to linear with $\angle(Ru-N-O) = 177.4(4)^\circ$. These values agree well with those of the ruthenium(II) Cp and Tp nitrosyl complexes.

**Summary and Prospects**

Many preparative and structural studies have demonstrated the versatility of the complexes [Ru(bdmpza)-(O2CR)(PPh3)] (2a, 2b) and [Ru(bdmpza)(O2C(CO)R)-(NO)(PPh3)] (3a-c) as 16 VE fragments with hemilabile $k^2$-coordinating carboxylato and 2-oxocarboxylato ligands.

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(41) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* 1974, 13, 339–406; Mononitrosyl complexes are described by [RuNO]$^+$, where $n$ is the number of d electron on ruthenium when the NO is formally bound as NO$^+$.  

Solvent molecules (pyridine, acetonitrile) as well as small molecules and ions (CO, SO₂, NO⁺) have been coordinated to a [Ru(bdmpza)(O₂CR)(PPh₃)] fragment. The chances of generating otherwise unstable compounds in the protecting environment of the new transition metal fragments seem quite promising. Future studies will be able to build on these results and might expand them to an activation of small molecules. Correlations between structure and reactivity are beginning to be recognized with a higher reactivity of the κ²-carboxylato complexes compared to that of the 2-oxocarboxylato complexes.

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**Supporting Information Available:** Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.