Behavior of (Ether−phosphine)ruthenium(II) Complexes [(η^6-C_6Me_6)RuH(P⌒O)][BF_4] Containing Reactive Ru−O and Ru−H Bonds toward Various Small Molecules and Their Application in Ring-Opening Metathesis Polymerization

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The ruthenium(II) complexes [(η^6-C_6Me_6)RuH(P⌒O)][BF_4] (**5a**−**c**; P⌒O = η^2-(*O*,*P*)-chelated ether−phosphine; **a**, $Ph_2PCH_2CH_2OCH_3$; **b**, $Ph_2PCH_2C_4H_7O_2$ ($C_4H_7O_2$ = 1,3-dioxanyl); **c**, $Ph_2PCH_2C_3H_5O_2$ ($C_3H_5O_2$ = 1,3-dioxolanyl)), each having a Ru−O and Ru−H functionality, were obtained by hydride abstraction from (η^6-C_6Me_6)RuH_2(P∼O) (**4a**−**c**, P∼O = η^1-(*P*)-coordinated ligand) with Ph_3CBF_4. A facile Ru−O bond cleavage occurs when **5a**−**c** are reacted with a variety of small molecules. Carbon monoxide, acetonitrile, *tert*-butyl isocyanide, and ethene were readily added to **5a**−**c**, leading to the corresponding adducts [(η^6-C_6Me_6)RuH(P∼O)L][BF_4] (**6a**−**c**, **7a**−**c**, **8a**−**c**, **10a**−**c**; L = CO, CH_3CN, *t*-BuNC, C_2H_4). π/σ rearrangements with incorporation of the Ru−H bonds in **10a**−**c** were not observed. If **5a**−**c** were treated with carbon disulfide, both functionalities were required. Rupture of the Ru−O contact resulted in a π-CS_2-coordinated intermediate followed by an insertion of CS_2 into the Ru−H bond to give the dithioformato complexes [(η^6-C_6Me_6)RuH(P∼O)(S_2CH)][BF_4] (**9a**−**c**). All compounds were obtained in excellent yields under mild conditions. The structures of **5a**, **7c**, **8c**, and **9a** were determined by single-crystal X-ray diffraction methods. Ring-opening metathesis polymerization of norbornene was achieved using complexes **5a**−**c** as the catalyst precursors.

Introduction

In recent years there has been considerable interest in the design and use of so-called hemilabile ligands.[1−3] They contain a soft donor (e.g., phosphorus) closely coordinated to the transition metal with a hard donor (e.g., oxygen) forming only a weak contact to the metal center. Due to this feature, the (ether)oxygen atom can easily be displaced by an incoming substrate. In addition, the oxygen function, which may be regarded as an intramolecular solvent, is able to stabilize a transition-metal fragment after substrate dissociation, and therefore, decomposition is suppressed.[2] Thus, ether−phosphines are capable of making available and protecting vacant coordination sites and lead to an improvement in both catalytic and stoichiometric reactions.[2,4]

The strength of the metal−oxygen bond in (ether−phosphine)ruthenium complexes depends on the O nucleophilicity of the ether moiety, the ring size of the cyclic ether, the number and position of the oxygen atoms in the ring, and the basicity at the ruthenium. These results were established from investigations of the fluxional behavior by VT ^{31}P NMR spectroscopy of octahedrally coordinated and half-sandwich ruthenium(II) complexes containing ether−phosphines as ligands.[5] According to these studies, complexes with $Ph_2PCH_2C_4H_7O_2$ ($C_4H_7O_2$ = 1,3-dioxanyl) (**2b**) have by far the lowest $\Delta H^{\ddagger}$ values while those with $Ph_2PCH_2C_3H_5O_2$ ($C_3H_5O_2$ = 1,3-dioxolanyl) (**2c**) and $Ph_2PCH_2CH_2OCH_3$ (**2a**) show nearly equal bond strengths.

This article reports the synthesis and reactivity of the complexes [(η^6-C_6Me_6)-RuH(P⌒O)][BF_4] (**5a**−**c**) (P⌒O, η^2-(*O*,*P*)-coordinated ether−phosphine) containing *two* concomitant functionalities.[6] Besides a metal−hydride

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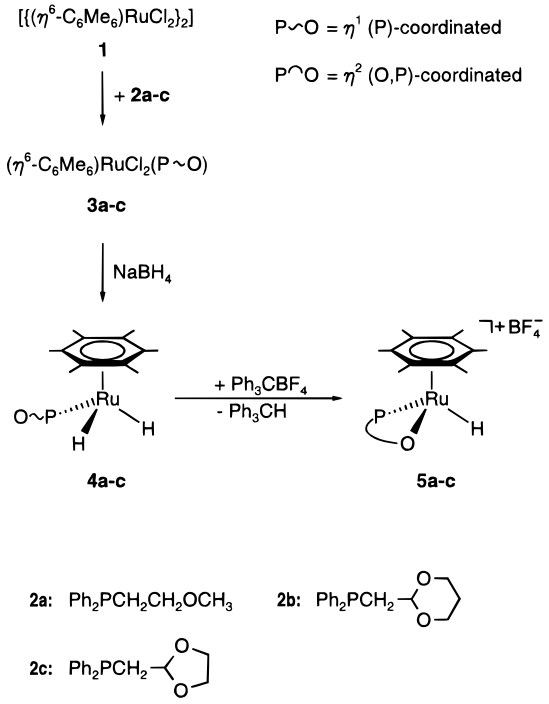
Scheme 1



bond, **5a**−**c** reveal each one reactive ruthenium−oxygen bond which is destabilized by the electron-donating properties of the π-coordinated hexamethylbenzene ring. By this means, two different types of reactions are discernible with small molecules. Carbon monoxide, acetonitrile, and *tert*-butyl isocyanide are activated under mild conditions just by cleavage of the ruthenium−oxygen function, whereas using carbon disulfide and olefins, both functionalities may be required. To investigate the dependence of the reactivity on the ether moieties employed, three different phosphines were introduced (Scheme 1). Complexes **5a**−**c** show also considerable activity in the ring-opening metathesis polymerization (ROMP) of norbornene.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were dried over the appropriate reagents and stored under argon. IR data were obtained with a Bruker IFS 48 FT-IR instrument. FD mass spectra were taken on a Finnigan MAT 711 A instrument (8 kV, 60 °C), modified by AMD; FAB mass spectra were recorded on a Finnigan MAT TSQ 70 (10 kV, 50 °C). Elemental analyses were performed with a Carlo Erba 1106 analyzer; Cl, F, and S analyses were carried out according to Schöniger[7] and determined as described by Dirscherl and Erne,[8] Brunisholz and Michot,[9] and Wagner.[10] Ru was analyzed according to the literature.[11] If not otherwise noted, the ^{1}H NMR measurements were performed with a Bruker DRX 250 spectrometer at 250.13 MHz. ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX 250 spectrometer at 101.25 and 62.90 MHz. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks, respectively. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 (δ = 0). If not otherwise mentioned, the NMR spectra were recorded at a temperature of 22 °C. The starting complex [{-(η^6-C_6Me_6)$RuCl_2$}$_2$] (**1**) was synthesized according to Bennett et al.[12] with a modification described by Crochet et al.[6c] The ether−phosphines **2a**−**c** were prepared as previously described.[13]

Dichloro(η^6-hexamethylbenzene)[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) (3a). A mixture of 1.40 g (2.09 mmol) of [{(η^6-C_6Me_6)$RuCl_2$}$_2$] (**1**) and 1.02 g (4.18 mmol) of the phosphine **2a** was stirred overnight in 50 mL of CH_2Cl_2. The reaction mixture was filtered (G3), and the filtrate was evaporated to dryness under reduced pressure. The residue was stirred in 100 mL of diethyl ether to give an orange powder, which was collected by filtration (G3) and dried in vacuo: yield 2.20 g (91%); mp 212 °C (dec); MS (FD, 60 °C) *m/e* 579 [M$^+$]. Anal. Calcd (Found) for $C_{27}H_{35}Cl_2OPRu$: C, 56.06 (55.79); H, 6.10 (6.02); Cl, 12.27 (12.30); Ru, 17.47 (17.39). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.7 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.3−128.3 (m, Ph), 96.6 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 68.9 (s, CH_2O), 58.2 (s, OCH_3), 30.0 (d, $^1J_{PC}$ = 29.6 Hz, PCH_2), 15.5 (s, C_6Me_6).

Dichloro[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](η^6-hexamethylbenzene)ruthenium(II) (3b). **3b** was similarly obtained by reacting 1.00 g (1.5 mmol) of **1** with 857 mg (3.0 mmol) of **2b** in 50 mL of CH_2Cl_2: yield 1.66 g (89%); mp 206 °C (dec); MS (FAB, 50 °C) *m/e* 620 [M$^+$]. Anal. Calcd (Found) for $C_{29}H_{37}Cl_2O_2PRu$: C, 56.13 (56.37); H, 6.01 (6.01); Cl, 11.43 (11.52); Ru, 16.29 (16.50). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.9 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.1−127.5 (m, Ph), 99.6 (s, CH), 96.0 (s, C_6Me_6), 66.1 (s, OCH_2CH_2) 34.5 (d, $^1J_{PC}$ = 37.7 Hz, PCH_2), 25.1 (s, OCH_2CH_2), 14.9 (s, C_6Me_6).

Dichloro[(1,3-dioxolan-2-ylmethyl)diphenylphosphine-*P*](η^6-hexamethylbenzene)ruthenium(II) (3c). **3c** was similarly obtained by reacting 1.10 g (1.64 mmol) of **1** with 896 mg (3.28 mmol) of **2c** in 50 mL of CH_2Cl_2: yield 1.80 g (90%); mp 209 °C (dec); MS (FD, 60 °C) *m/e* 606 [M$^+$]. Anal. Calcd (Found) for $C_{28}H_{35}Cl_2O_2PRu$: C, 55.45 (55.24); H, 5.82 (5.69); Cl, 11.69 (11.73); Ru, 16.66 (16.68). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.3−127.6 (m, Ph), 101.8 (d, $^2J_{PC}$ = 6.1 Hz, CH), 96.0 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 64.1 (s, OCH_2), 32.1 (d, $^1J_{PC}$ = 28.3 Hz, PCH_2), 15.1 (s, C_6Me_6).

(η^6-Hexamethylbenzene)dihydrido[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) (4a). A mixture of 2.00 g (3.46 mmol) of **3a** and 980 mg (25.95 mmol) of $NaBH_4$ in 50 mL of 2-propanol was heated under reflux for 45 min. The brown suspension was allowed to cool to room temperature and was evaporated to dryness under reduced pressure. The brown residue was extracted with 80 mL of toluene, and the solution was then filtered (G3). The filtrate was reduced to a volume of 15 mL, transferred to a neutral alumina column (length of column 5 cm), and finally eluted with toluene. The yellow eluate was evaporated to dryness, and the residue was washed with 20 mL of *n*-hexane to give a pale yellow precipitate, which was collected by filtration (G3) and dried under reduced pressure to yield 1.16 g (66%) of **4a**; mp 92 °C (dec); MS (FD, 60 °C) *m/e* 508 [M$^+$ − 2H]. Anal. Calcd (Found) for $C_{27}H_{37}OPRu$: C, 63.63 (63.45); H, 7.32 (7.32); Ru, 19.83 (20.01). IR (KBr, cm^{-1}): ν(RuH) 1949 (s). ^{31}P{^{1}H} NMR

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(C_6D_6): δ 53.1 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.9−128.0 (m, Ph), 97.1 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 71.2 (d, $^2J_{PC}$ = 12.1 Hz, CH_2O), 58.6 (s, OCH_3), 36.0 (d, $^1J_{PC}$ = 30.3 Hz, PCH_2), 18.2 (s, C_6Me_6). ^1H NMR (C_6D_6): δ −11.0 (d, $^2J_{PH}$ = 45.3 Hz, 2H, RuH).

[(1,3-Dioxan-2-ylmethyl)diphenylphosphine-*P*](η^6-hexamethylbenzene)dihydridoruthenium(II) (4b). **4b** was synthesized and worked up in the same way as **4a** by using 1.50 g (2.42 mmol) of **3b** and 686 mg (18.1 mmol) of $NaBH_4$ in 50 mL of 2-propanol: yield 907 mg (68%); mp 115 °C (dec); MS (FD, 60 °C) *m/e* 551 [M^+]. Anal. Calcd (Found) for $C_{29}H_{39}O_2PRu$: C, 63.14 (62.98); H, 7.13 (7.03); Ru, 18.32 (18.18). IR (KBr, cm^{-1}): ν(RuH) 1931 (s). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 55.3 (s). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 141.6−127.1 (m, Ph), 102.4 (d, $^2J_{PC}$ = 11.5 Hz, CH), 96.5 (d, $^2J_{PC}$ = 3.4 Hz, C_6Me_6), 66.6 (s, OCH_2CH_2), 40.8 (d, $^1J_{PC}$ = 29.6 Hz, PCH_2), 25.9 (s, OCH_2CH_2), 17.6 (s, C_6Me_6). ^1H NMR (toluene-d_8): δ −11.0 (d, $^2J_{PH}$ = 45.3 Hz, 2H, RuH).

[(1,3-Dioxolan-2-ylmethyl)diphenylphosphine-*P*](η^6-hexamethylbenzene)dihydridoruthenium(II) (4c). **4c** was synthesized and worked up in the same way as **4a** by using 1.50 g (2.47 mmol) of **3c** and 702 mg (18.5 mmol) of $NaBH_4$ in 50 mL of 2-propanol: yield 864 mg (65%); mp 119 °C (dec); MS (FD, 60 °C) *m/e* 536 [M^+ − 2H]. Anal. Calcd (Found) for $C_{28}H_{37}O_2PRu$: C, 62.55 (62.76); H, 6.94 (6.84); Ru, 18.80 (18.97). IR (KBr, cm^{-1}): ν(RuH) 1946 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 54.6 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 133.4−127.2 (m, Ph), 104.3 (d, $^2J_{PC}$ = 10.1 Hz, CH), 96.8 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 64.4 (s, OCH_2), 40.6 (d, $^1J_{PC}$ = 30.3 Hz, PCH_2), 17.7 (s, C_6Me_6). ^1H NMR (C_6D_6): δ −10.8 (d, $^2J_{PH}$ = 45.7 Hz, 2H, RuH).

(η^6-Hexamethylbenzene)hydrido[(methoxyethyl)diphenylphosphine-*O,P*]ruthenium(II) Tetrafluoroborate (5a). A mixture of 1.30 g (2.55 mmol) of **4a** and 842 mg (2.55 mmol) of Ph_3CBF_4 in 50 mL of THF was stirred overnight at room temperature. The yellow solution was evaporated to dryness under reduced pressure, and the residue was extracted with *n*-hexane in a Soxhlet apparatus. The resulting yellow powder was dried in vacuo: yield 1.44 g (95%): mp 107 °C (dec); MS (FD, 60 °C) *m/e* 508 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{27}H_{36}BF_4OPRu$: C, 54.46 (54.47); H, 6.09 (5.76); F, 12.76 (13.17); Ru, 16.96 (16.73). IR (KBr, cm^{-1}): ν(RuH) 1943 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 67.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.2−127.1 (m, Ph), 98.6 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 79.3 (s, CH_2O), 72.4 (s, OCH_3), 30.5 (d, $^1J_{PC}$ = 27.6 Hz, PCH_2), 16.4 (s, C_6Me_6). ^1H NMR (CD_2Cl_2): δ −8.3 (d, $^2J_{PH}$ = 46.3 Hz, 1H, RuH).

[(1,3-Dioxan-2-ylmethyl)diphenylphosphine-O,P](η^6-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (5b). **5b** was prepared and worked up analogously to **5a** by using 820 mg (1.48 mmol) of **4b** and 491 mg (1.48 mmol) of Ph_3CBF_4 in 50 mL of THF: yield 830 mg (88%); mp 111 °C (dec); MS (FD, 60 °C) *m/e* 551 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{29}H_{38}BF_4O_2PRu$: C, 54.64 (54.82); H, 6.01 (6.19); F, 11.92 (12.18); Ru, 15.85 (16.12). IR (KBr, cm^{-1}): ν(RuH) 2001 (m, br). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 65.8, 49.9 (both s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.6−127.4 (m, Ph), 107.8, 105.1 (s, CH), 98.9, 98.6 (s, C_6Me_6), 80.8, 76.9 (s, $RuOCH_2CH_2$), 67.6, 66.9 (s, OCH_2CH_2), 37.5, 36.6 (d, $^1J_{PC}$ = 24.5 and 28.9 Hz, PCH_2), 26.9, 22.0 (s, OCH_2CH_2), 16.6 (s, C_6Me_6).

[(1,3-Dioxolan-2-ylmethyl)diphenylphosphine-O,P](η^6-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (5c). **5c** was prepared and worked up analogously to **5a** by using 850 mg (1.58 mmol) of **4c** and 522 mg (1.58 mmol) of Ph_3CBF_4 in 50 mL of THF: yield 867 mg (90%); mp 94 °C (dec); MS (FD, 60 °C) *m/e* 537 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{28}H_{36}BF_4O_2PRu$: C, 53.94 (54.06); H, 5.82 (5.72); F, 12.19 (12.34); Ru, 16.21 (16.19). IR (KBr, cm^{-1}): ν(RuH) 1978 (w, br). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): major diastereomer, δ 60.2 (s); minor diastereomer, δ 55.7 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135.8−127.8 (m, Ph of both diastereomers); major diastereomer, δ 110.1 (d, $^2J_{PC}$ = 8.1 Hz, CH), 99.0 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 75.7 (s, $Ru-OCH_2$), 66.1 (s, OCH_2), 36.0 (d, $^1J_{PC}$ = 26.3 Hz, PCH_2), 16.5 (s, C_6Me_6); minor diastereomer, δ 109.5 (d, $^2J_{PC}$ = 10.1 Hz, CH), 98.6 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 70.6 (s, $Ru-OCH_2$), 66.7 (s, OCH_2), 33.6 (d, $^1J_{PC}$ = 27.6 Hz, PCH_2), 16.7 (s, C_6Me_6). ^1H NMR (400.14 MHz, CD_2Cl_2): major diastereomer, δ −8.2 (d, $^2J_{PH}$ = 46.1 Hz, RuH); minor diastereomer, δ −8.4 (d, $^2J_{PH}$ = 48.0 Hz, RuH).

Carbonyl(η^6-hexamethylbenzene)hydrido[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) Tetrafluoroborate (6a). A solution of **5a** (120 mg, 0.20 mmol) in 10 mL of CH_2Cl_2 was treated with carbon monoxide (1 bar) at ambient temperature. After 1 h, the orange solution changed to bright yellow. The reaction mixture was reduced to a volume of 1 mL and was layered with diethyl ether (3 mL) to afford bright yellow crystals of **6a**: yield 81 mg (65%); mp 148 °C (dec); MS (FD, 60 °C) *m/e* 537 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{28}H_{36}BF_4O_2PRu$: C, 53.94 (54.07); H, 5.82 (5.77); F, 12.19 (12.10); Ru, 16.21 (15.86). IR (KBr, cm^{-1}): ν(RuH) 2059 (s), ν(CO) 1973 (vs). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.6 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 198.7 (d, $^2J_{PC}$ = 18.9 Hz, CO), 132.5−127.2 (m, Ph), 113.3 (s, C_6Me_6), 67.5 (s, CH_2O), 58.5 (s, OCH_3), 31.2 (d, $^1J_{PC}$ = 34.6 Hz, PCH_2), 16.5 (s, C_6Me_6). ^1H NMR (CD_2Cl_2): δ −11.0 (d, $^2J_{PH}$ = 31.3 Hz, 1H, RuH).

Carbonyl[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](η^6-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (6b). **6b** was synthesized and worked up in the same way as **6a** by reacting a solution of 150 mg (0.24 mmol) of **5b** in 10 mL of CH_2Cl_2 with carbon monoxide (1 bar) for 30 min: yield 109 mg (68%); mp 142 °C (dec); MS (FD, 60 °C) *m/e* 579 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{30}H_{38}BF_4O_3PRu$: C, 54.15 (54.22); H, 5.76 (5.61); F, 11.42 (11.79); Ru, 15.19 (14.87). IR (KBr, cm^{-1}): ν(RuH) 2068 (m), ν(CO) 1974 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 199.3 (d, $^2J_{PC}$ = 20.6 Hz, CO), 134.9−127.5 (m, Ph), 113.7 (d, $^2J_{PC}$ = 1.4 Hz, C_6Me_6), 99.0 (d, $^2J_{PC}$ = 4.3 Hz, CH), 67.1 (d, $^4J_{PC}$ = 6.4 Hz, OCH_2CH_2), 36.0 (d, $^1J_{PC}$ = 34.9 Hz, PCH_2), 22.9 (s, OCH_2CH_2), 17.2 (s, C_6Me_6). ^1H NMR (CD_2Cl_2): δ −11.0 (d, $^2J_{PH}$ = 31.0 Hz, 1H, RuH).

Carbonyl[(1,3-dioxolan-2-ylmethyl)diphenylphosphine-*P*](η^6-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (6c). **6c** was synthesized and worked up in the same way as **6a** by reacting a solution of 130 mg (0.21 mmol) of **5c** in 10 mL of CH_2Cl_2 with carbon monoxide (1 bar) for 3 h: yield 84 mg (62%); mp 124 °C (dec); MS (FAB 50 °C) *m/e* 565 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{29}H_{36}BF_4O_3PRu$: C, 53.47 (53.22); H, 5.57 (5.62); F, 11.67 (11.53); Ru, 15.51 (15.32). IR (KBr, cm^{-1}): ν(RuH) 2060 (m), ν(CO) 1973 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.2 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 199.2 (d, $^2J_{PC}$ = 21.6 Hz, CO), 132.7−129.1 (m, Ph), 113.7 (s, C_6Me_6), 100.9 (s, CH), 65.2 (d, $^4J_{PC}$ = 12.8 Hz, OCH_2), 35.7 (d, $^1J_{PC}$ = 30.7 Hz, PCH_2), 17.2 (s, C_6Me_6). ^1H NMR (CD_2Cl_2): δ −11.0 (d, $^2J_{PH}$ = 31.9 Hz, 1H, RuH).

Acetonitrile(η^6-hexamethylbenzene)hydrido[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) Tetrafluoroborate (7a). A solution of **5a** (150 mg, 0.25 mmol) in 10 mL of CH_2Cl_2 was treated with 10.3 mg (0.25 mmol) of acetonitrile at room temperature. The orange solution spontaneously brightens to yellow. After 5 min of stirring, the solvent was removed under vacuum. The residue was washed with 10 mL of *n*-hexane to give a pale yellow precipitate, which was collected by filtration (G3) and dried in vacuo: yield 159 mg (100%); mp 148 °C (dec); MS (FD, 60 °C) *m/e* 548 [M^+ − BF_4]. Anal. Calcd (Found) for $C_{29}H_{39}BF_4NOPRu$: C, 54.73 (54.41); H, 6.18 (6.03); F, 11.94 (12.06); N, 2.20 (2.22); Ru, 15.88 (16.05). IR (KBr, cm^{-1}): ν(CN) 2278 (w), ν(RuH) 1946 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.9 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.4−127.8 (m, Ph), 123.6 (s, NCMe), 101.6 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 68.3 (d, $^2J_{PC}$ = 6.1 Hz, CH_2O), 58.3 (s, OCH_3), 29.6 (d, $^1J_{PC}$ = 32.3 Hz, PCH_2), 16.4 (s, C_6Me_6), 3.4 (s, NC*Me*). ^1H NMR (CD_2Cl_2): δ −9.6 (d, $^2J_{PH}$ = 45.3 Hz, 1H, RuH).

Acetonitrile[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](η⁶-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (7b). **7b** was prepared and worked up analogously to **7a** by treating a solution of 180 mg (0.28 mmol) of **5b** in 10 mL of CH_2Cl_2 with 11.6 mg (0.28 mmol) of CH_3CN: yield 190 mg (100%); mp 83 °C (dec); MS (FD, 60 °C) *m/e* 593 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{31}H_{42}BF_4NO_2PRu$: C, 54.88 (55.10); H, 6.09 (5.79); F, 11.20 (11.08); N, 2.06 (2.10); Ru, 14.90 (15.09). IR (KBr, cm^{-1}): *ν*(CN) 2275 (w), *ν*(RuH) 1948 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 48.2 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 133.1−127.2 (m, Ph), 123.5 (s, N*C*Me), 101.6 (d, $^2J_{PC}$ = 2.9 Hz, C_6Me_6), 99.8 (d, $^2J_{PC}$ = 5.0 Hz, CH), 66.9 (d, $^2J_{PC}$ = 3.4 Hz, O*C*H_2CH$_2$), 35.8 (d, $^1J_{PC}$ = 32.7 Hz, PCH$_2$), 25.1 (s, OCH$_2$*C*H$_2$), 16.6 (s, C_6*Me*$_6$), 3.3 (s, NC*Me*).^{1}H NMR (CD_2Cl_2): *δ* −9.6 (d, $^2J_{PH}$ = 35.5 Hz, 1H, RuH).

Acetonitrile[(1,3-dioxolan-2-ylmethyl)diphenylphosphine-*P*](η⁶-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (7c). **7c** was prepared and worked up analogously to **7a** by treating a solution of 160 mg (0.26 mmol) of **5c** in 10 mL of CH_2Cl_2 with 10.5 mg (0.26 mmol) of CH_3CN: yield 170 mg (100%); mp 165 °C (dec); MS (FD, 60 °C) *m/e* 579 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{30}H_{39}BF_4NO_2PRu$: C, 54.23 (54.16); H, 5.92 (5.60); F, 11.44 (11.63); N, 2.11 (2.00); Ru, 15.21 (14.98). IR (KBr, cm^{-1}): *ν*(CN) 2278 (w), *ν*(RuH) 1949 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 46.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 133.0−128.4 (m, Ph), 124.2 (s, N*C*Me), 102.1 (d, $^2J_{PC}$ = 5.4 Hz, CH), 102.0 (d, $^2J_{PC}$ = 2.7 Hz, C_6Me_6), 65.1 (d, $^2J_{PC}$ = 5.4 Hz, OCH$_2$), 35.2 (d, $^1J_{PC}$ = 31.0 Hz, PCH$_2$), 16.5 (s, C_6*Me*$_6$), 3.7 (s, NC*Me*).^{1}H NMR (CD_2Cl_2,): *δ* −9.6 (d, $^2J_{PH}$ = 45.3 Hz, 1H, RuH).

***tert*-Butyl Isocyanide(η⁶-hexamethylbenzene)hydrido[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) Tetrafluoroborate (8a).** Addition of *t*-BuNC (27.9 mg, 0.35 mmol) to a solution of **5a** (200 mg, 0.35 mmol) in 10 mL of dichloromethane, followed by 5 min of stirring at room temperature, gave a yellow solution, which was evaporated to dryness. The residue was washed with 10 mL of *n*-hexane to give a bright yellow precipitate. The precipitate was collected by filtration (G3), washed with 10 mL of *n*-hexane, and dried in vacuo: yield 228 mg (100%); mp 207 °C (dec); MS (FD, 60 °C) *m/e* 592 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{32}H_{45}BF_4NOPRu$: C, 56.64 (56.27); H, 6.68 (6.56); F, 11.20 (11.08); N, 2.06 (2.30); Ru, 14.89 (14.92). IR (KBr, cm^{-1}): *ν*(CN) 2138 (vs), *ν*(RuH) 1974 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 49.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 148.8 (d, $^2J_{PC}$ = 18.9 Hz, *C*NCMe$_3$), 134.1−127.8 (m, Ph), 107.2 (d, $^2J_{PC}$ = 2.8 Hz, C_6Me_6), 68.3 (d, $^2J_{PC}$ = 7.1 Hz, CH$_2$O), 58.4 (s, OCH$_3$), 57.6 (s, CN*C*Me$_3$), 30.3 (d, $^1J_{PC}$ = 32.7 Hz, PCH$_2$), 30.1 (s, CNC*Me*$_3$), 16.4 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* −11.2 (d, $^2J_{PH}$ = 36.1 Hz, 1H, RuH).

***tert*-Butyl Isocyanide[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](η⁶-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (8b).** **8b** was prepared and worked up analogously to **8a** by using a solution of 180 mg (0.28 mmol) of **5b** in 10 mL of CH_2Cl_2 and 23.5 mg (0.28 mmol) of *t*-BuNC: yield 201 mg (100%); mp 193 °C (dec); MS (FD, 60 °C) *m/e* 635 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{34}H_{47}BF_4NO_2PRu$: C, 56.67 (56.89); H, 6.57 (6.45); F, 10.54 (10.84); N, 1.94 (2.05); Ru, 14.03 (14.12). IR (KBr, cm^{-1}): *ν*(CN) 2142 (s), *ν*(RuH) 1985 (w). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 50.0 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 142.9 (s, *C*NCMe$_3$), 133.9−127.2 (m, Ph), 107.3 (d, $^2J_{PC}$ = 2.1 Hz, C_6Me_6), 99.6 (d, $^2J_{PC}$ = 4.3 Hz, CH), 66.9 (d, $^4J_{PC}$ = 13.5 Hz, O*C*H_2CH$_2$), 57.6 (s, CN*C*Me$_3$), 36.5 (d, $^1J_{PC}$ = 32.7 Hz, PCH$_2$), 30.1 (s, CNC*Me*$_3$), 25.1 (s, OCH$_2$*C*H$_2$), 16.6 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* −11.2 (d, $^2J_{PH}$ = 35.6 Hz, 1H, RuH).

***tert*-Butyl Isocyanide[(1,3-dioxolan-2-ylmethyl)diphenylphosphine-*P*](η⁶-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (8c).** **8c** was prepared and worked up analogously to **8a** by using a solution of 190 mg (0.30 mmol) of **5c** in 10 mL of CH_2Cl_2 and 25.3 mg (0.30 mmol) of *t*-BuNC: yield 215 mg (100%); mp 201 °C (dec); MS (FD, 60 °C) *m/e* 620 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{33}H_{45}BF_4NO_2PRu$: C, 56.10 (55.80); H, 6.42 (6.31); F, 10.76 (11.03); N, 1.98 (2.07); Ru, 14.30 (14.19). IR (KBr, cm^{-1}): *ν*(CN) 2139 (vs), *ν*(RuH) 1983 (w). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 48.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 148.6 (d, $^2J_{PC}$ = 18.2 Hz, *C*NCMe$_3$), 133.1−128.2 (m, Ph), 107.4 (d, $^2J_{PC}$ = 2.0 Hz, C_6Me_6), 101.6 (d, $^2J_{PC}$ = 5.4 Hz, CH), 64.8 (d, $^4J_{PC}$ = 6.0 Hz, OCH$_2$), 57.5 (s, CN*C*Me$_3$), 35.3 (d, $^1J_{PC}$ = 31.7 Hz, PCH$_2$), 30.1 (s, CNC*Me*$_3$), 16.6 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* −11.1 (d, $^2J_{PH}$ = 36.5 Hz, 1H, RuH).

η²-Dithioformato(η⁶-hexamethylbenzene)[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) Tetrafluoroborate (9a). A solution of **5a** (200 mg, 0.36 mmol) in 10 mL of CH_2Cl_2 was treated with 51.1 mg (0.72 mmol) of carbon disulfide at room temperature. Within 60 min the solution turned from orange to dark red. After the solution was stirred overnight, the solvent was removed under reduced pressure. The residue was washed with 10 mL of *n*-hexane and dried in vacuo: yield 225 mg (100%); mp 78 °C (dec); MS (FAB, 50 °C) *m/e* 585 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{28}H_{36}BF_4OPRuS_2$: C, 50.08 (49.92); H, 5.40 (5.21); F, 11.32 (11.03); Ru, 15.05 (14.99); S, 9.55 (9.73). IR (KBr, cm^{-1}): *δ* (HCS$_2$) 1288 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 33.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 242.5 (d, $^3J_{PC}$ = 7.4 Hz, CS$_2$), 134.2−127.2 (m, Ph), 102.6 (d, $^2J_{PC}$ = 2.0 Hz, C_6Me_6), 68.3 (d, $^2J_{PC}$ = 2.7 Hz, CH$_2$O), 58.3 (s, OCH$_3$), 25.9 (d, $^1J_{PC}$ = 29.6 Hz, PCH$_2$), 16.6 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* 11.7 (d, $^4J_{PH}$ = 6.3 Hz, 1H, HCS$_2$).

[(1,3-Dioxan-2-ylmethyl)diphenylphosphine-*P*](η²-dithioformato)(η⁶-hexamethylbenzene)ruthenium(II) Tetrafluoroborate (9b). **9b** was obtained analogously as **9a** by using a solution of **5b** (200 mg, 0.31 mmol) in 10 mL of CH_2Cl_2 and 47.8 mg (0.62 mmol) of CS_2: yield 224 mg (100%); mp 79 °C (dec); MS (FD, 60 °C) *m/e* 626 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{30}H_{38}BF_4O_2PRuS_2$: C, 50.49 (50.64); H, 5.67 (5.37); F, 10.65 (10.91); Ru, 14.16 (14.34); S, 8.99 (9.32). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 32.2 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 242.6 (d, $^3J_{PC}$ = 6.7 Hz, CS$_2$), 135.6−124.4 (m, Ph), 102.9 (s, C_6Me_6), 99.6 (s, CH), 66.5 (s, O*C*H_2CH$_2$), 33.2 (d, $^1J_{PC}$ = 30.3 Hz, PCH$_2$), 23.5 (s, OCH$_2$*C*H$_2$), 16.0 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* 11.6 (d, $^4J_{PH}$ = 6.3 Hz, 1H, HCS$_2$).

[(1,3-Dioxolan-2-ylmethyl)diphenylphosphine-*P*](η²-dithioformato)(η⁶-hexamethylbenzene)ruthenium(II) Tetrafluoroborate (9c). **9c** was obtained analogously by using a solution of **5c** (180 mg, 0.29 mmol) in 10 mL of CH_2Cl_2 and 44.0 mg (0.58 mmol) of CS_2: yield 202 mg (100%); mp 76 °C (dec); MS (FD, 60 °C) *m/e* 613 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{29}H_{36}BF_4O_2PRuS_2$: C, 49.79 (50.07); H, 5.19 (5.40); F, 10.86 (10.64); Ru, 14.47 (14.70); S, 9.17 (9.02). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 30.9 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 243.0 (d, $^3J_{PC}$ = 8.0 Hz, CS$_2$), 133.9−127.8 (m, Ph), 117.1 (d, $^2J_{PC}$ = 2.0 Hz, C_6Me_6), 103.0 (d, $^2J_{PC}$ = 2.0 Hz, CH), 65.2 (s, OCH$_2$), 31.1 (d, $^1J_{PC}$ = 30.0 Hz, PCH$_2$), 16.4 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* 11.7 (d, $^4J_{PH}$ = 6.3 Hz, 1H, HCS$_2$).

(η²-Ethene)(η⁶-hexamethylbenzene)hydrido[(methoxyethyl)diphenylphosphine-*P*]ruthenium(II) Tetrafluoroborate (10a). A solution of 140 mg (0.24 mmol) of **5a** in 10 mL of CH_2Cl_2 was treated with ethene (1 bar) at ambient temperature. After 8 h of stirring, the solvent was removed under reduced pressure. The residue was washed with 10 mL of *n*-hexane to give a pale beige precipitate, which was collected by filtration (G3) and dried in vacuo: yield 146 mg (100%); mp 73 °C (dec); MS (FD, 60 °C) *m/e* 537 [$M^+ - BF_4$]. Anal. Calcd (Found) for $C_{29}H_{40}BF_4OPRu$: C, 55.87 (55.78); H, 6.47 (6.26); F, 12.19 (12.07); Ru, 16.21 (16.40). IR (KBr, cm^{-1}): *ν*(RuH) 2029 (w). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* 53.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C): *δ* 131.9−127.0 (m, Ph), 108.9 (d, $^2J_{PC}$ = 2.0 Hz, C_6Me_6), 67.9 (s, CH$_2$O), 58.3 (s, OCH$_3$), 41.0, 37.6 (s, C_2H_4), 29.1 (d, $^1J_{PC}$ = 37.1 Hz, PCH$_2$), 15.9 (s, C_6*Me*$_6$). ^{1}H NMR (CD_2Cl_2): *δ* −10.9 (d, $^2J_{PH}$ = 36.9 Hz, 1H, RuH).

Table 1. Crystal Data and Refinement Details for Compounds 5a, 7c, 8c, and 9a

	compound			
	5a	**7c**	**8c**	**9a**
formula	$C_{27}H_{36}BF_4OPRu$	$C_{30}H_{39}BF_4NO_2PRu$	$C_{33}H_{45}BF_4NO_2PRu$	$C_{28}H_{36}BF_4OPRuS_2$
fw	595.4	664.5	706.6	671.5
color	yellow cubes	pale yellow cubes	yellow cubes	red cubes
cryst dimens	0.25 × 0.20 × 0.15	0.35 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.40 × 0.30 × 0.30
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a, Å	11.714(3)	9.883(3)	9.768(2)	8.632(2)
b, Å	13.097(3)	12.773(3)	12.018(2)	15.857(4)
c, Å	18.019(3)	12.924(3)	14.577(2)	10.622(3)
α, deg	90	76.65(2)	105.28(3)	90
β, deg	108.03(1)	69.51(2)	90.66(3)	96.38(2)
γ, deg	90	87.70(2)	90.50(3)	90
V, Å^3	2628.7(10)	1485.5(7)	1650.5(6)	1444.9(7)
Z	4	2	2	2
d_{calcd}, g cm^{-3}	1.504	1.486	1.422	1.543
T, °C	−100	−100	−100	−100
F(000), e	1224	684	732	688
μ(Mo Kα), mm^{-1}	0.704	0.635	0.576	0.79
2θ limits, deg	4−50	4−50	4−50	4−50
no. of reflns measd	10 078	10 386	11 490	10 186
no. of unique data with $I \geq 2\sigma(I)$	3266	5000	5218	4984
no. of variables	321	378	389	343
S	1.67	1.67	1.59	0.94
R_1[a]	0.042	0.032	0.050	0.020
wR_2[b]	0.105	0.081	0.130	0.055

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

[(1,3-Dioxan-2-ylmethyl)diphenylphosphine-*P*](η²-ethene)(η⁶-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (10b). **10b** was prepared and worked up analogously by reacting a solution of **5b** (150 mg, 0.24 mmol) in 10 mL of CH_2Cl_2 with ethene (1 bar) for 1 h: yield 156 mg (100%); mp 178 °C (dec); MS (FD, 60 °C) *m/e* 579 [M$^+$ − BF_4]. Anal. Calcd (Found) for $C_{31}H_{42}BF_4O_2PRu$: C, 55.95 (55.73); H, 6.36 (6.12); F, 11.42 (11.79); Ru, 15.87 (16.08). IR (KBr, cm^{-1}): ν(RuH) 2032 (w). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 52.3 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 133.0−126.2 (m, Ph), 109.7 (d, $^2J_{PC}$ = 3.1 Hz, C_6Me_6), 99.4 (s, CH), 67.1 (d, $^2J_{PC}$ = 6.3 Hz, OCH_2-CH_2), 40.8, 37.7 (s, br, C_2H_4), 36.3 (d, $^1J_{PC}$ = 25.1 Hz, PCH_2), 25.0 (s, OCH_2CH_2), 16.0 (s, C_6Me_6).^1H NMR (CD_2Cl_2): δ −10.8 (d, $^2J_{PH}$ = 36.5 Hz, 1H, RuH).

[(1,3-Dioxolan-2-ylmethyl)diphenylphosphine-*P*](η²-ethene)(η⁶-hexamethylbenzene)hydridoruthenium(II) Tetrafluoroborate (10c). **10c** was prepared and worked up analogously by reacting a solution of **5c** (140 mg, 0.22 mmol) in 10 mL of CH_2Cl_2 with ethene (1 bar) for 16 h: yield 146 mg (100%); mp 130 °C (dec); MS (FD, 60 °C) *m/e* 564 [M$^+$ − BF_4]. Anal. Calcd (Found) for $C_{30}H_{40}BF_4O_2PRu$: C, 55.31 (55.03); H, 6.19 (5.87); F, 11.66 (11.31); Ru, 15.51 (15.83). IR (KBr, cm^{-1}): ν(RuH) 2029 (w, br). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 51.7 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 132.9−128.0 (m, Ph), 109.9 (d, $^2J_{PC}$ = 2.0 Hz, C_6Me_6), 101.7 (s, CH), 65.2 (d, $^2J_{PC}$ = 4.0 Hz, OCH_2), 41.5, 38.5 (s, br, C_2H_4), 34.6 (d, $^1J_{PC}$ = 34.4 Hz, PCH_2), 16.4 (s, C_6Me_6).^1H NMR (CD_2Cl_2): δ −10.8 (d, $^2J_{PH}$ = 34.8 Hz, 1H, RuH).

ROMP of Norbornene with Complexes 5a−c as Catalyst Precurscors. In a typical experiment, a solution of approximately 1 wt % (referring to the weight of norbornene) of the corresponding complex **5a**−**c** in 2 mL of CH_2Cl_2 was added to a solution of norbornene in CH_2Cl_2 (10 mg of monomer/1 mL of solvent), and the solution was stirred at room temperature. Within 60 min the solution became viscous. After the corresponding reaction time (Table 6) the mixture was added to 500 mL of methanol and the resulting mixture was vigorously stirred for 2 h. The colorless precipitate was collected by filtration (G3), washed with methanol, and dried in vacuo.

Crystallographic Analyses. Single crystals of **5a**, **7c**, **8c**, and **9a** were obtained by slow diffusion of *n*-hexane into concentrated solutions of **5a**, **7c**, **8c**, and **9a** in CH_2Cl_2. The crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo Kα radiation. Rotation photographs were taken, and a photo search was performed to find a suitable reduced cell. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters for **5a**, **7c**, **8c**, and **9a** are summarized in Table 1. Intensities were collected with the ω-scan technique with the scan speed varying from 6 to 60 deg/min in ω. Scan ranges for **5a**, **7c**, **8c**, and **9a** were 1.0, 1.2, 1.2, and 1.0, respectively. For compounds **8c** and **9a**, an absorption correction was applied (Ψ-scan, maximum and minimum transmission **8c**, 0.547, 0.480; **9a**, 0.563, 0.520). All structures were solved by Patterson methods[14] and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms (based on F^2). The hydride atoms of compounds **5a** and **7c** were located from a final Fourier map and refined with isotropic thermal parameters, while all other hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference syntheses were 1.124 and −0.625 (**5a**), 1.492 and −0.503 (**7c**), 1.343 and −0.723 (**8c**), and 0.328 and −0.340 e Å^3 (**9a**).

Results and Discussion

The dihydrido complexes **4a**−**c** were obtained upon replacing both chlorides by hydrides in the intermediates **3a**−**c** with $NaBH_4$[15] which result from the reaction of [{(η^6-C_6Me_6)$RuCl_2$}$_2$] (**1**) with the ligands **2a**−**c** (Scheme 1).[16] The pale yellow, air-sensitive compounds **4a**−**c** were characterized by their ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR and mass spectra (Experimental Section). Moreover, the structure of **4b** was determined by an X-ray structural analysis.[17]

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(16) (a) *Comprehensive Organometallic Chemistry II*; Able, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 7, Chapter 9. (b) Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163.

Synthesis of the η^2(O,P)-Chelated Hydridoruthenium(II) Complexes [(η^6-C_6Me_6)RuH(P⌒O)][BF_4] (5a−c). Intramolecular coordination of the ether oxygen donors succeeded by treating **4a−c** with Ph_3CBF_4 in THF, leading to the bifunctionalized, yellow complexes [(η^6-C_6Me_6)RuH(P⌒O)][BF_4] (**5a−c**), which are easily soluble in CH_2Cl_2 but insoluble in nonpolar solvents (Scheme 1).

Because of the ring contribution Δ_R,[18] the ^{31}P resonance (δ 67.5) of **5a** is shifted to lower field compared to the corresponding signal of **4a**. The η^2-(*O,P*)-coordination mode of the phosphines in complexes **5b,c** is responsible for a center of chirality at the carbon atom of the CH unit of the ether moiety. Since ruthenium represents an additional center of chirality, complexes **5b,c** may exist in diastereomeric forms. Whereas in similar examples only one diastereomeric form was observed,[19,20] the $^{31}P\{^1H\}$ NMR spectra of **5b,c** in CD_2Cl_2 show two singlets at 65.8 and 49.9 ppm for **5b** and at 60.2 and 55.7 ppm for **5c** in an approximately 1:1 and 3:1 ratio, which is consistent with the existence of two diastereomers. In contrast to the remarkable low-field shift in case of **5a**, the ring contribution Δ_R in **5b,c** is obviously compensated by steric contributions to the chemical shift.[20,21]

Compared to **4a−c** in the $^{13}C\{^1H\}$ NMR spectra of **5a−c**, the signals (doubled sets in the case **5b,c** because of diastereomers!) of the carbon atoms adjacent to the ether oxygen function are shifted to lower field,[22] which is a further hint for the η^2-(*O,P*)-coordination mode. In the high-field region (ca. −8 ppm) of the ^1H NMR spectra of **5a** and **5c,** one doublet ($^2J_{PH}$) and two doublets (diasteromers!), respectively, are assigned to the hydrides. However, even in the 400 MHz ^1H NMR spectrum of **5b** only two broad resonances occur, consistent with two superimposed doublets.

Crystal Structure of 5a. For a full characterization of the chelates **5a−c**, an X-ray structural analysis has been performed with the example of complex **5a**. The ORTEP drawing of the cation of **5a** is depicted in Figure 1. A listing of selected bond distances and angles is compiled in Table 2. **5a** adopts a three-legged pianostool configuration with an O(1)−Ru(1)−P(1) bond angle of 82.77(10)°. The Ru(1)−P(1) bond length (2.266(1) Å) corresponds well with the Ru−P distance of the η^2-(*O,P*)-coordinated ether−phosphine in [(η^5-C_5Me_5)Ru(P∼O)(P⌒O)][BPh_4], 2.258(3) Å.[20] However, in contrast to the related complex [(η^6-$C_6H_3Me_3$)RuCl(P⌒O)][BPh_4] (O,P = $Ph_2PCH_2CH_2OCH_3$)[23] in which the five-membered chelate ring prefers an envelope conformation, **5a** reveals a twisted chelate ring. The atoms C(25) and C(26) are located −0.25 Å below and 0.38 Å above the plane that is formed by the atoms P(1), Ru(1), and O(1). Compared to the mesitylene and half-sandwich complexes [(η^6-$C_6H_3Me_3$)RuCl(P⌒O)][BPh_4][23] and [(η^5-C_5Me_5)Ru(P⌒O)L][BPh_4] (L = CO, 2.231 (3) Å; P∼O, 2.262 (6) Å),[4b,20] respectively, the distance between ruthenium and oxygen (Ru(1)−O(1) = 2.188 (3) Å) is shorter.

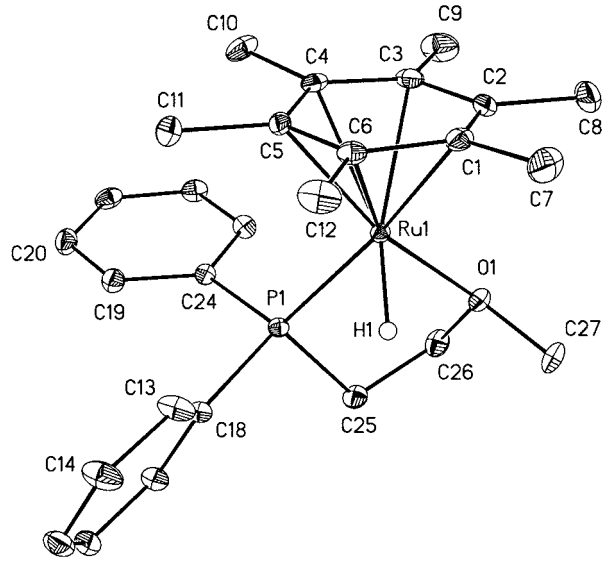

Figure 1. ORTEP plot of **5a**.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 5a

Bond Lengths			
Ru(1)−O(1)	2.188(3)	P(1)−C(25)	1.847(5)
Ru(1)−P(1)	2.2656(12)	C(25)−C(26)	1.509(8)
O(1)−C(27)	1.450(6)	C(26)−O(1)	1.448(6)
Bond Angles			
O(1)−Ru(1)−P(1)	82.77(10)	O(1)−C(26)−C(25)	111.6(4)
C(25)−P(1)−Ru(1)	102.9(2)	C(26)−O(1)−Ru(1)	115.3(3)
C(26)−C(25)−P(1)	108.9(3)	C(26)−O(1)−C(27)	112.0(4)

Utilization of Only One Functionality: Cleavage of the Ru−O Bond in 5a−c by Reaction with CO, CH_3CN, and *t*-BuNC. If the complexes [(η^6-C_6Me_6)-RuH(P⌒O)][BF_4] (**5a−c**) are reacted with carbon monoxide, acetonitrile, and *tert*-butyl isocyanide, a facile Ru−O bond dissociation takes place, resulting in the formation of the yellow adducts [(η^6-C_6Me_6)RuH(P∼O)L][BF_4] (L = CO (**6a−c**), CH_3CN (**7a−c**), *t*-BuNC (**8a−c**), Scheme 2).

Compared to **5a−c**, in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of **5−8** the ^{31}P signals and ^{13}C resonances of the carbon atoms in the α-position of the ether oxygen function are shifted to higher field, confirming the η^1-(*P*)-coordination of the O,P ligands. The ^{31}P signals split into doublets if the non-hydride protons are selectively decoupled, corroborating the presence of one hydride. The IR spectra of **6−8** reveal typical absorptions for the C≡O and C≡N stretching vibrations (Experimental Section).[24,25]

Crystal Structures of 7c and 8c. Complexes **7c** and **8c** were characterized by crystal structure determinations as well (Figures 2 and 3). Selected bond distances and angles are summarized in Tables 3 and 4. The overall geometry is similar to that of other three-

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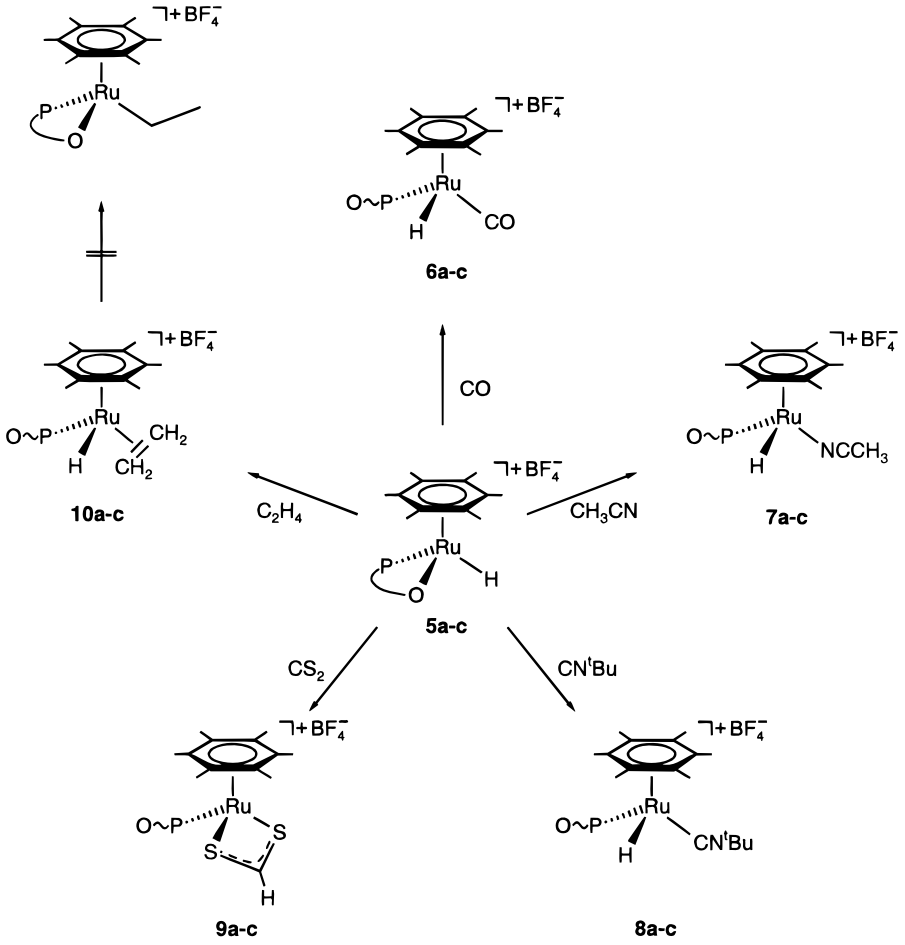
Scheme 2



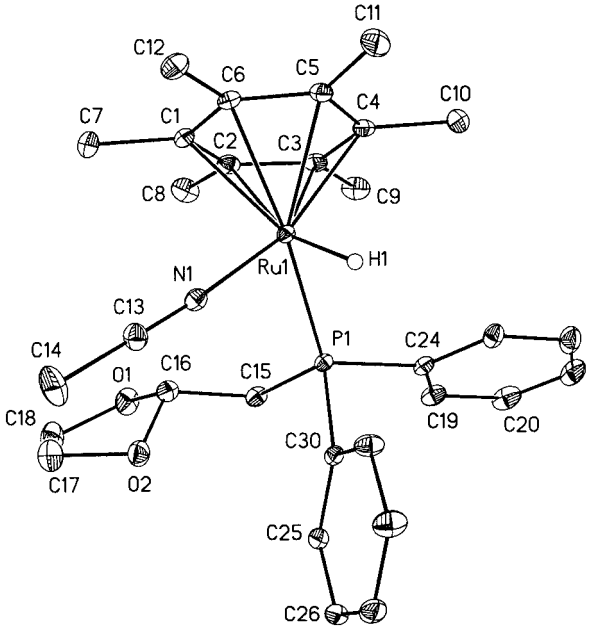


Figure 2. ORTEP plot of **7c**.

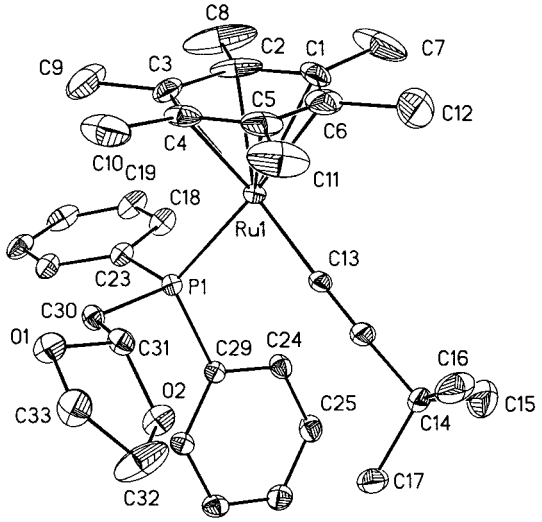


Figure 3. ORTEP plot of **8c**.

legged piano-stool analogues.[26] The Ru(1)−N(1) distance in **7c** (2.032(2) Å) is slightly shorter than that in $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_2Cl][BF_4]$ (2.062(5) Å)[27] and $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_3][PF_6]_2$ (2.055(4) Å).[28] The Ru−$NCCH_3$ and Ru−CN-*t*-Bu arrangements in **7c** and **8c** deviate only slightly from a stretched geometry. The bond lengths N(1)−C(13) (1.145(4) Å), C(13)−C(14) (1.461(4) Å) and Ru(1)−C(13) (1.925(4) Å), C(13)−N(1) (1.160(6) Å) are similar to those established in the above-mentioned ruthenium complexes[27,28] and in $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)(ICH_3)][PF_6]$, respectively.[29]

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 7c

Bond Lengths			
Ru(1)−N(1)	2.032(2)	N(1)−C(13)	1.145(4)
Ru(1)−P(1)	2.2895(9)	C(13)−C(14)	1.461(4)
Bond Angles			
N(1)−Ru(1)−P(1)	86.45(6)	N(1)−C(13)−C(14)	178.3(3)
C(13)−N(1)−Ru(1)	172.4(2)		

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for 8c

Bond Lengths			
Ru(1)−C(13)	1.925(4)	N(1)−C(13)	1.160(6)
Ru(1)−P(1)	2.2810(11)	N(1)−C(14)	1.448(6)
Bond Angles			
C(13)−Ru(1)−P(1)	86.60(11)	N(1)−C(13)-Ru(1)	177.5(3)
C(13)−N(1)−C(14)	177.6(5)		

Utilization of Two Functionalities: Reactions with Carbon Disulfide and Olefins. Five minutes after an excess of CS_2 was reacted with **5a**−**c** in CH_2Cl_2 at ambient temperature, the ^{31}P signals of the chelates disappeared and two new single peaks appeared between 32 and 36 ppm. The low-field signal is indicative of an intermediary π-coordinated carbon disulfide being formed by rupture of the weak Ru−O bond.[30] This was also evidenced by an IR absorption at 1306 cm^{-1} (**5a**/CS_2, CH_2Cl_2), pointing to the C═S vibration.[31] Finally, in the ^1H NMR spectrum of a mixture of **5a**/CS_2, a doublet at − 1.7 ppm is still ascertained, belonging to the Ru−H proton of the intermediate.

Gradually, the above-mentioned low-field ^{31}P resonance in the spectra of **5a**−**c**/CS_2 disappears, because in a following step CS_2 is inserted into the Ru−H bond of the intermediates to give the red, air-stable products **9a**−**c** (Scheme 2). The intensity of the high-field ^{31}P signal attributed to the $HCS_2Ru(P{\sim}O)$ moiety increases and remains the only resonance after completion of the reaction. The IR absorption at 1306 cm^{-1} is replaced by a band at 1288 cm^{-1}, which is characteristic for ν_{as} (CS_2) of **9a**.

Crystal Structure of 9a. To confirm the insertion of carbon disulfide into the Ru−H bond, an X-ray structural analysis has been performed with the example of **9a** (Figure 6). Selected bond distances and angles are summarized in Table 5. Complex **9a** is octahedrally coordinated about the ruthenium with the C_6Me_6 ligand occupying three coordination sites. The distorted octahedral geometry is due to a small S(1)−Ru(1)−S(2) angle of 71.41(2)°, similar to those in the corresponding ruthenium and osmium dithioformato complexes.[30,32] Both almost equal Ru−S bonds are comparable with reported values.[32]

Stirring a solution of **5a**−**c** in dichloromethane under an atmosphere of ethene affords the pale beige adducts [(η^6-C_6Me_6)RuH(η^2-C_2H_4)(P∼O)][BF_4] (**10a**−**c**, Scheme 2). In agreement with an η^1-(*P*)-coordination of the O,P ligands, the $^{31}P\{^1H\}$ NMR spectra of **10a**−**c** each exhibit a singlet between 52 and 55 ppm. At ambient temperature, the $^{13}C\{^1H\}$ NMR spectra of **10b,c** display two broad resonances at 37 and 42 ppm, corresponding to the ethene carbon atoms. In the case of **10a**, these signals appear only at −30 °C. Obviously, the rotation of the olefin in the complexes with the sterically more demanding ether−phosphines **2b,c** is slow on the NMR time scale at room temperature. The same dynamic behavior in **10a** is already observed at −30 °C, whereas at room temperature the ethylene signals coalesce into the baseline.

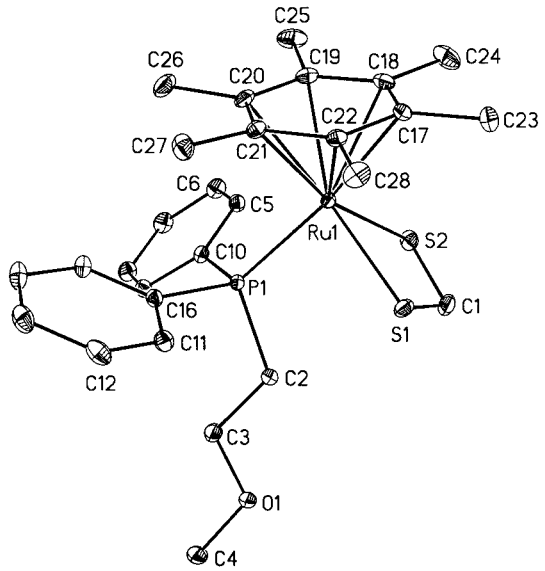

Figure 4. ORTEP plot of **9a**.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for 9a

Bond Lengths			
Ru(1)−P(1)	2.3476(9)	S(1)−C(1)	1.675(3)
Ru(1)−S(1)	2.3814(9)	S(2)−C(1)	1.672(3)
Ru(1)−S(2)	2.3649(7)		
Bond Angles			
P(1)−Ru(1)−S(1)	91.31(2)	S(2)−C(1)−S(1)	111.71(14)
P(1)−Ru(1)−S(2)	89.46(3)	C(1)−S(1)−Ru(1)	88.06(9)
S(2)−Ru(1)−S(1)	71.41(2)	C(1)−S(2)−Ru(1)	88.68(10)

At about −11 ppm a doublet is observed in the ^1H NMR spectra of **10a**−**c** ($^2J_{PH} \approx 35$ Hz) which is ascribed to the hydride ligand.[33] Unlike in [(η^6-C_6H_6)RuH(η^2-C_2H_4)(PMe_3)][PF_6],[34] the Ru−H function in **10a**−**c** is *not* involved in a π/σ rearrangement. The results of an X-ray structural analysis of **10a** are in good agreement with those of a similar complex.[35]

Because of the remarkable tolerance of ruthenium complexes toward a variety of functionalized olefins, ruthenium-based systems play an important role in the ring-opening metathesis reaction.[36,37] It was reported that the presence of Ru−H bonds in a complex is

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(35) Pautz, S. Ph.D. Thesis, University of Tübingen, 1997. Monoclinic, space group C_c, unit cell dimensions $a = 18.124(2)$ Å, $b = 11.059(2)$ Å, $c = 16.052(3)$ Å, $\beta = 118.071(12)°$; $Z = 4$, $V = 2838.8(8)$ Å^3, $d_{calc} = 1.459$ g cm^{-3}.
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Scheme 3

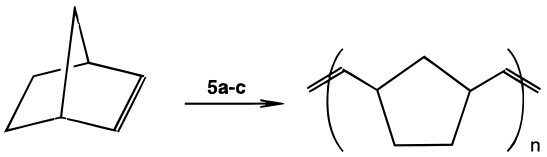

Table 6. Polymerization of Norbornene with Compounds 5a−c

complex	time (h)	mg of norbornene/ mL of CH_2Cl_2	yield (%)[a]	activity[b]	trans[c] (%)
5a	1	10	14.5	82.0	78.1
		30	36.5	224.7	82.1
5a	2	10	28.1	82.4	83.2
		30	45.7	134.3	82.9
5a	4	10	58.4	73.4	85.2
		30	56.3	73.4	81.7
5a	8	10	78.6	52.3	83.5
		30	60.2	42.9	80.9
5a	16	10	80.7	28.3	83.5
		30	74.2	25.1	78.1
5b	16	10	35.2	10.0	82.6
5c	16	10	53.5	19.6	83.0

[a] Methanol-insoluble fraction. [b] Activity = [g of polymer/(g of Ru)(h)]. [c] Cis and trans double bonds of the polymer were quantified by inverse-gated decoupled ^{13}C NMR spectrospcopy.

advantageous for the generation of active metathesis catalysts.[36] This observation in connection with the application of (arene)ruthenium complexes in ring-opening metathesis reactions[38] were motivations to prove the potential of the chelates **5a**−**c** in the ROMP of norbornene. If a CH_2Cl_2 solution of norbornene is treated with catalytic amounts of **5a**−**c** at room temperature, a polymerization is induced and the reaction mixture becomes viscous within 1 h. Finally, (poly)-norbornene was isolated by precipitation with methanol as a white, tacky polymer (Scheme 3). The results of the ring-opening metathesis polymerization of norbornene with **5a**−**c** are summarized in Table 6.

Conclusion

The investigations presented describe the synthesis of the complexes $[(\eta^6\text{-}C_6Me_6)RuH(P\frown O)][BF_4]$ (**5a**−**c**), which are provided with each one having a functional Ru−O and Ru−H bond, and their behavior toward small molecules. With carbon monoxide, acetonitrile, and *tert*-butyl isocyanide, only the Ru−O contact is affected. In the reaction of **5a**−**c** with carbon disulfide, both functionalities participate. In the beginning, a rupture of the Ru−O linkage takes place with π-coordination of CS_2, subsequently carbon disulfide is inserted into the Ru−H bond. The second step is favored by an increasing steric demand of the employed ether−phosphine. Since the basic character of the selected phosphines is too low,[34] no π/σ rearrangement happens when **5a**−**c** are treated with ethene.

A remarkable dependence of the qualitatively estimated reaction rates on the kind of ether−phosphines was ascertained in the systems **5a**−**c**/CO and ethene. In both instances the time required for quantitative formation of the corresponding adducts **6a**−**c** and **10a**−**c** increases in the order **2b** < **2a** < **2c** (Experimental Section). For **2b**, this finding is consistent with the lowest energy of the Ru−O bond. However, other influences, e.g., steric factors, are also likely to account for the different kinetics of the above-mentioned reactions because the $\Delta H^{\ddagger}$ values for **2a** and **2c** are rather similar.

Complexes **5a**−**c** turned out to be suitable catalyst precursors for the ring-opening metathesis polymerization of norbornene. Their considerable activities increase with a decreasing steric demand of the phosphine employed in the sequence **2b** < **2c** < **2a**, pointing to the fact that the Ru−O bond cleavage which happens in the initiation phase of the reaction is only of minor significance for the overall catalytic process.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **5a**, **7a**, **8c**, and **9a** (26 pages). Ordering information is given on any current masthead page.

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