Synthesis, Molecular Structure and Reactions of Stable Square-Planar 16-Electron Ruthenium(0) Complexes: *trans*-[RuCl(NO)$(PR_3)_2$]☆

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The reduction of $[RuCl_3(NO)(PPh_3)_2]$ (**1**) with Zn/Cu generates $[RuCl(NO)(PPh_3)_2]$ that by ligand exchange with PR_3 (R_3 = *i*Pr_3, *i*Pr_2Ph) affords the stable 16-electron ruthenium(0) complexes *trans*-$[RuCl(NO)(PR_3)_2]$ (**2**, **3**). The X-ray structural analysis of **2** confirmed the square-planar geometry around the metal center. HCl oxidatively adds to **2** and **3** to give the octahedral ruthenium(II) compounds $[RuHCl_2(NO)(PR_3)_2]$ (**4**, **5**). On treatment of **2** and **3** with CO, TCNE, CH_2 (generated from CH_2N_2) and O_2, five-coordinate 1:1 adducts $[RuCl(NO)(L)(PR_3)_2]$ (**6**–**12**) are formed. The dioxygen complexes **11** and **12** react with SO_2 to afford the sulfatoruthenium(II) derivatives $[RuCl(NO)\{\eta^2(O,O)\text{-}O_2SO_2\}(PR_3)_2]$ (**13**, **14**). Compound **13** (R_3 = P*i*Pr_3) has been characterized by X-ray structural analysis.

Numerous isolable transition-metal complexes for rhodium(I), of the general composition $[ML_4]$ (L = monodentate ligand) with a 16-electron configuration, are known[1]. In contrast, examples of corresponding isoelectronic ruthenium(0) compounds are extremely rare. Four-coordinate species such as $[Ru(CO)_4]$[2], $[Ru(PMe_3)_4]$[3] or $[(\eta^6\text{-}C_6H_6)Ru(P\mathit{i}Pr_3)]$[4], which have been generated in situ, either oligomerize to $[Ru_3(CO)_{12}]$ or react by intramolecular C–H activation to give hydridoruthenium(II) derivatives. Most remarkably, however, Caulton et al. recently reported the isolation of the 16-electron compound $[Ru(CO)_2(P\mathit{t}Bu_2Me)_2]$ that was prepared by reduction of *cis,cis,trans*-$[RuCl_2(CO)_2(P\mathit{t}Bu_2Me)_2]$ with activated Mg turnings in THF with 80% yield[5]. This coordinatively unsaturated ruthenium(0) complex has a non-planar geometry and can be viewed as a fragment of a trigonal bipyramid from which an equatorial ligand is removed[5]. The structure of $[Ru(CO)_2(P\mathit{t}Bu_2Me)_2]$ is markedly different to that of the matrix-isolated chelate compounds $[Ru(R_2PCH_2CH_2PR_2)_2]$ (R = Me, Et, Ph), which based on the UV spectroscopic data are thought to be almost square-planar[6]. Formally related to Caulton's compound is the olefin complex $[Ru(CH_2{=}CHPh)_2(PPh_3)_2]$ in which one of the styrene ligands, however, shows evidence of a η^3 bonding mode[7].

Following our recent work on the preparation of the isolable osmium(0) compounds *trans*-$[OsCl(NO)(P\mathit{i}Pr_2R)_2]$ (R = *i*Pr, Ph)[8], we were interested to find out whether analogous ruthenium complexes are also accessible. Already in 1969, Stiddard and Townsend[9] described the generation of the extremely reactive and air-sensitive nitrosylruthenium(0) species $[RuCl(NO)(PPh_3)_2]$ from $[RuCl_3(NO)(PPh_3)_2]$ (**1**) and Zn/Cu which reacts with $PMePh_2$ and PMe_2Ph by ligand exchange to give the corresponding $[RuCl(NO)(PR_3)_2]$ derivatives[10]. Since attempts to isolate these compounds failed, we decided to use more bulky phosphines for our studies and apply a strategy similar to that which had been successful in osmium chemistry. Here we report the synthesis of stable square-planar 16-electron ruthenium(0) complexes, the X-ray crystal structure of one of these, and we illustrate that the reactivity of the analogous nitrosylosmium(0) and -ruthenium(0) compounds, at least in some respects, is strikingly different.

Preparation and Molecular Structure of $[RuCl(NO)(P\mathit{i}Pr_2R)_2]$

The synthetic route to obtain the target compounds **2** and **3** (Scheme 1) is similar to that used by Stone[10] for the in situ generation of the corresponding $PMePh_2$ and PMe_2Ph derivatives. Treatment of **1** with Zn/Cu in benzene, followed (after filtration of excess of the reducing agent) by addition of P*i*Pr_3 or P*i*Pr_2Ph and stirring of the reaction mixture for 30 min at 80 °C resulted in the formation of green crystalline **2**, **3** in 65–70% yield. Both compounds are extremely air-sensitive and thermally unstable. Therefore, they can be stored only under argon below −15 °C for a few days. Compounds **2** and **3** readily dissolve in aromatic hydrocarbons (benzene, toluene), are insoluble in pentane and hexane, and slowly decompose in presence of CH_2Cl_2 or $CHCl_3$. The ^{1}H-NMR spectra, which for **2** show *one* and for **3** (due to prochirality of the phosphorus atoms) *two* doublets of virtual triplets for the $PCHCH_3$ protons, are in agreement with a square-planar configuration involving transoid phosphane ligands. This is equally supported by the ^{31}P-NMR spectra of **2** and **3** in which only one sharp singlet is observed.

The structural proposal shown in Scheme 1 has been substantiated by the X-ray crystal structure analysis of **2**. As shown in Figure 1, both the N–Ru–Cl and P–Ru–P units

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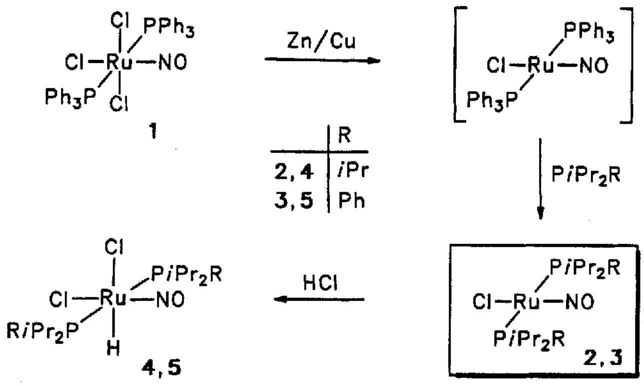
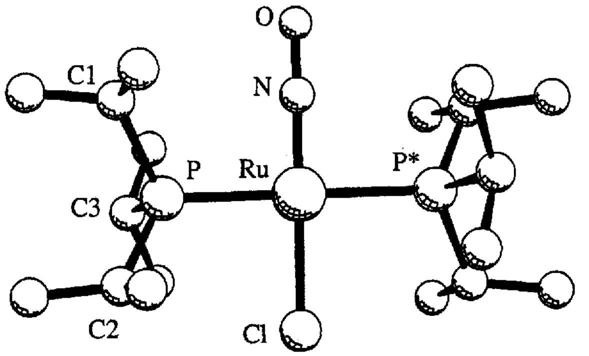


are almost linear with Ru–P, Ru–N and Ru–Cl distances in the expected range. Since the ruthenium atom (like osmium in the isostructural compound *trans*-[OsCl(NO)(P-iPr$_3$)$_2$][8]) lies on a crystallographic center of symmetry, a 1:1 disorder of the chloro and nitrosyl ligands results; this is also characteristic for a variety of square-planar rhodium(I) and iridium(I) complexes containing [MCl(PiPr$_3$)$_2$] as a molecular unit[11]. We note, however, that due to the symmetry-based disorder, the Ru–N, Ru–Cl and N–O bond lengths of **2** possess a higher grade of uncertainty than apparent in the estimated standard deviations.

Figure 1. Molecular structure of **2**; selected bond lengths [Å] and angles [°]: Ru–Cl 2.333(1), Ru–N 1.686(4), Ru–P 2.397(1), N–O 1.187(6); Cl–Ru–P 89.57(4), Cl–Ru–N 179.0(2), P–Ru–N 89.9(1), Ru–N–O 179.2(5)



Addition and Oxidative Addition Reactions of 2 and 3

While the isoelectronic compound *trans*-[RhCl(CO)-(PiPr$_3$)$_2$][11a,12] is rather inert toward CO, CNR, CH_2N_2 etc., the related ruthenium complex **2** as well as the PiPr$_2$Ph analogue **3** react not only with Lewis acids but also with Lewis bases. In both cases, five- or six-coordinate products are obtained, which have an 18-electron configuration at the metal center.

The reactions of **2** and **3** with HCl in benzene proceed quite smoothly and give the expected hydridodichlororuthenium(II) complexes **4** and **5** nearly quantitatively. Both are orange crystalline solids for which, due to the appearance of one sharp singlet in the ^{31}P-NMR spectra, a transoid arrangement of the two phosphanes in the octahedral coordination sphere is proposed. Since both the nitrosyl and the hydrido ligand exert a strong *trans* influence, we assume that for **4** and **5** the configuration shown in Scheme 1, with the chlorides in *cis* position, is preferred. Surprisingly, both **2** and **3** are completely inert toward H_2 at 1 atm and room temperature. This is in marked contrast to the behaviour of the osmium analogues *trans*-[OsCl(NO)(PiPr$_2$R)$_2$] (R = iPr, Ph), which on treatment with H_2 afford the corresponding dihydridoosmium(II) derivatives[8].

An almost instantaneous reaction occurs on treatment of **2** and **3** with CO in benzene at 5 °C. In less than one minute the yellow-brownish air-stable monocarbonyl complexes **6** and **7** (Scheme 2) are formed and isolated in 90–95% yield. Identical to the starting materials (**2**, **3**) and the hydrido compounds (**4**, **5**), the ^{31}P-NMR spectra of **6** and **7** also display only one ^{31}P-NMR resonance and thus the four stereoisomers **A–D** (Figure 2) could exist. From these stereoisomers, we consider **D** as being unlikely due to the *trans* disposition of the two strong π-acceptor ligands CO and NO. For five-coordinate ruthenium(0) complexes the trigonal-bipyramidal configuration in general seems to be favored[13]; this has also been confirmed by X-ray structural analysis of the carbene(nitrosyl)ruthenium(0) and -osmium(0) derivatives [MCl(NO)(=CX$_2$)(PPh$_3$)$_2$] (M = Ru, Os; X = H, F)[14]. Since we know, however, from our work on analogous 16-electron aryl(chloro)- and vinyl(chloro)metal compounds of iridium[15] and osmium[16], that the energy difference between the trigonal-bipyramidal and the square-pyramidal geometry is probably quite small, predictions about which of the stereoisomers (**A**, **B** or **C**) is preferred in the case of **6** and **7** should be made with great caution.

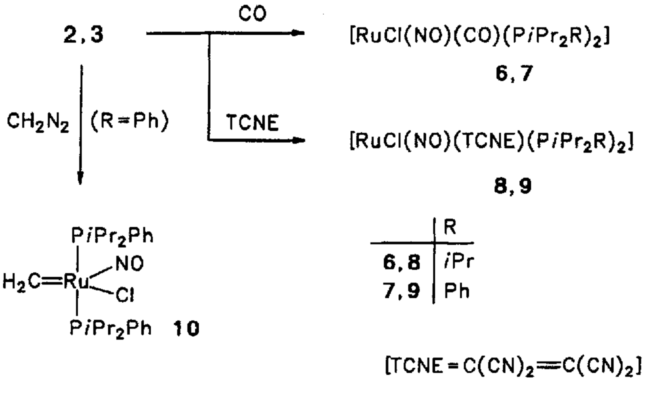
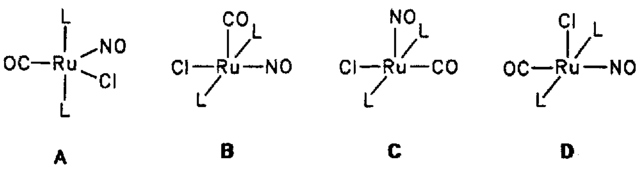


Figure 2. Possible stereoisomers of compounds **6** and **7** with *trans*-disposed phosphane ligands (L = PiPr$_3$, PiPr$_2$Ph)



The reactivity of **2** and **3** toward olefinic hydrocarbons depends crucially on the type of olefin used. While ethene possibly forms an extremely labile 1:1 adduct (indicated by a change of colour from green to orange by passing a stream of C_2H_4 through a solution of **2** or **3** in benzene) which, however, could neither be isolated nor correctly identified, with tetracyanoethene (TCNE) stable complexes **8** and **9** are obtained. The IR spectra of **8** and **9** show one sharp ν(CN) band at about 2225 cm^{-1} indicating that the TCNE ligand is coordinated via the C=C bond and not via the lone pair of one of the CN groups. This proposal is in agreement with the ^{13}C-NMR data, the most typical feature of which is the appearance of only *one* resonance for the C=C and *one* for the CN carbon atoms. With regard to the structure of **8** and **9**, we consider a trigonal-bipyramidal (tbp) geometry with the tetracyanoethene lying in the equatorial plane as most likely. If we take the equivalence of the phosphane ligands into account, the two stereoisomers **E** and **F** shown in Figure 3 are possible. Since the IR spectroscopic data of **8** and **9** and of the related 1:1 adducts of $[RuCl(NO)(PPh_3)_2]$ and TCNE or (*E*)-$C_2H_2(CN)_2$ are quite similar[17] and since the latter probably have a tbp configuration with the two phosphanes in *cis* and the nitrosyl and chloro ligands in *trans* disposition, the stereoisomer **E** seems to be preferred. This is also in agreement with the structure of the five-coordinate iridium complex $[IrCl(CO)(TCNE)(PPh_3)_2]$, which has been substantiated by X-ray structural analysis[18].

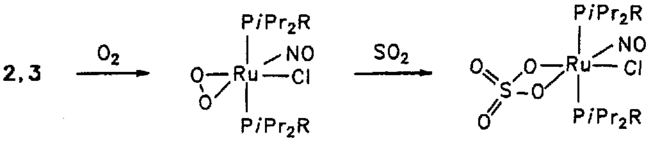
Figure 3. Possible stereoisomers of compounds **8** and **9** with chemically equivalent phosphane ligands (L = P*i*Pr_3, P*i*Pr_2Ph)

E F

Unexpectedly, the behaviour of **2** and **3** toward diazomethane is distinctly different. While compound **2** is rather inert and even on warming does not react with CH_2N_2 to give a five-coordinate adduct, the reaction of **3** with diazomethane in toluene/ether at 0 °C proceeds quite rapidly and affords the carbene complex **10** in moderate to good yields. The off-white crystalline solid is air-stable and its properties resembles those of the analogous bis(triphenylphosphane)ruthenium(0) compounds $[RuCl(NO)(=CHR)(PPh_3)_2]$ (R = H, Et)[14a,19]. As far as the NMR spectroscopic data are concerned, characteristic features are the low-field signal for the CH_2 protons at $\delta = 13.71$ in the ^1H NMR and for the corresponding CH_2 carbon atom at $\delta = 205.4$ in the ^{13}C-NMR spectrum. Since not only the NMR but also the IR data, in particular the position of the ν(NO) vibration, are in good agreement with those of $[OsCl(NO)(=CH_2)(PPh_3)_2]$[14a] and $[OsCl(NO)(=CH_2)(PiPr_2R)_2]$[8], we assume that **10** also has a trigonal-bipyramidal geometry.

Ru(η^2-O_2) Complexes and Their Conversion to Ru(η^2-O_2SO_2) Derivatives

Despite the decomposition of numerous trialkylphosphaneruthenium(0) compounds in the presence of air, both starting materials **2** and **3** react with dry oxygen in benzene to yield the O_2 adducts **11** and **12** (Scheme 3) nearly quantitatively. The brown products, which are stable as solids, slowly decompose in solution to give the corresponding phosphanoxides OP*i*Pr_2R. The IR spectra of **11** and **12** display, besides the strong NO stretching frequency at about 1755 cm^{-1}, a characteristic band at 870 (**11**) and 866 cm^{-1} (**12**), which is assigned to the ν(O_2) vibration of the dioxygen ligand. Comparison with reference data[20] leave no doubt that a side-on coordination of the O_2 unit exists.



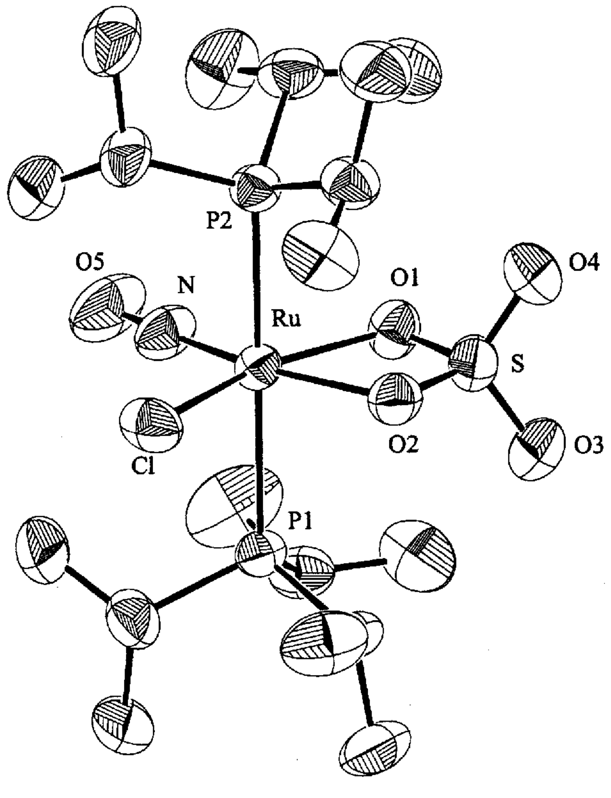
11,12 **13,14**

	R
11,13	*i*Pr
12,14	Ph

In order to test the oxidizing capabilities of the Ru(O_2) compounds, the behaviour toward SO_2 has been investigated. Both **11** and **12** react almost instantaneously with SO_2 in toluene to give the sulfatoruthenium(II) derivatives **13** and **14** in about 60–65% yield. **11** and **12** thus resemble some other d^8 transition-metal complexes, which on treatment with SO_2 also afford sulfatometal compounds[21]. In the IR spectra of **13** and **14** four ν(SO) vibrations appear between 1300 and 850 cm^{-1} indicating a pseudo-C_{2v} symmetry of the SO_4 unit with a bidentate linkage of the sulfato ligand via two oxygens to the metal.

A single-crystal X-ray diffraction investigation of **13** confirms the structural proposal shown in Scheme 3. The ORTEP plot (Figure 4) reveals that the geometry around the ruthenium(II) center is nearly octahedral with the two phosphines *trans* to each other. The sulfato ligand is distorted tetrahedral with O–S–O-bond angles lying between 99° and 115°. The distances from sulfur to the terminal oxygen atoms of the SO_4 unit [1.427(4) and 1.441(4) Å] are ca. 0.1 Å shorter than those to the coordinated oxygens [1.528(4) and 1.547(4) Å] and almost indentical to the length of the S=O double bond [1.432 Å][22]. The angle O1–Ru–O2 [68.3(2)°] is very similar to that of other M(η^2-O_2SO_2) complexes[21,23] and considerably larger than the bite angle of related carboxylatoruthenium(II) derivatives[24]. Both the P–Ru–P and Ru–N–O axes are nearly linear; the angle P1–Ru–P2 [173.82(5)°] deviates somewhat more from linearity than that in the analogous bis(triphenylphosphane) compound[23]. The distance Ru–O2 [2.073(5) Å] is slightly shorter than the distance Ru–O1 [2.098(3) Å], which we contribute to the *trans* influence of the NO ligand.

Figure 4. Molecular structure of **13**; selected bond lengths [Å] and angles [°]: Ru–Cl 2.343(1), Ru–N 1.709(5), Ru–P1 2.511(1), Ru–P2 2.514(1), Ru–O1 2.098(3), Ru–O2 2.073(5), N–O5 1.162(6), S–O1 1.528(4), S–O2 1.547(4), S–O3 1.427(4), S–O4 1.441(4); O1–Ru–O2 68.3(2), Cl–Ru–N 99.2(2), Cl–Ru–P1 87.36(4), Cl–Ru–P2 87.73(4), Cl–Ru–O1 161.2(1), Cl–Ru–O2 92.8(1), N–Ru–P1 91.8(2), N–Ru–P2 92.7(2), N–Ru–O1 99.6(2), N–Ru–O2 167.9(2), P1–Ru–P2 173.82(5), P1–Ru–O1 91.8(1), P1–Ru–O2 88.5(1), P2–Ru–O1 91.7(1), P2–Ru–O2 88.0(1), Ru–N–O5 176.1(7), Ru–O1–S 96.0(2), Ru–O2–S 96.4(2), O1–S–O2 99.3(2), O1–S–O3 111.1(3), O1–S–O4 110.6(3), O2–S–O3 110.9(3), O2–S–O4 109.2(3), O3–S–O4 114.6(3)



Conclusion

In this work, the preparation and structural characterisation of stable square-planar d^8 ruthenium(0) complexes of general composition *trans*-[RuCl(NO)(PR$_3$)$_2$] (**2**, **3**) has been described. These electronically and coordinatively unsaturated compounds not only oxidatively add Broensted acids such as HCl but also react with Lewis bases to form 1:1 adducts. In some respects, however, the reactivity of **2** and **3** is markedly different from that of the analogous osmium(0) complexes *trans*-[OsCl(NO)(P*i*Pr$_2$R)$_2$] (R = *i*Pr, Ph), the latter being much more reactive toward H_2 than the ruthenium counterparts. This difference is surprising insofar as in general the order of reactivity is 4d > 5d (e.g., Ru > Os; Rh > Ir; etc.) which makes ruthenium, rhodium and palladium compounds, for example, more appropriate for catalytic studies than the corresponding osmium, iridium or platinum analogues. Work in progress is aimed to find out whether the chemical behaviour of [RuX(NO)(PR$_3$)$_2$] complexes can be manipulated by replacing chloride for acetate, acetylacetonate etc., an exchange which has been very useful for performing various oxidative addition and insertion reactions in related rhodium(I) chemistry[25].

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Experimental

All operations were carried out under argon with the Schlenk-tube technique. The starting materials **1**[26] and P*i*Pr$_2$Ph[27] were prepared by published procedures. P*i*Pr$_3$ is a commercial product from Strem. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400; vt = virtual triplet [$N = {}^3J$(PH) + ${}^5J$(PH) or ${}^1J$(PC) + ${}^3J$(PC)]. – MS: Varian MAT CH7.

1. Preparation of trans-[RuCl(NO)(PiPr$_3$)$_2$] (**2**): A solution of 902 mg (1.18 mmol) of **1** in 40 ml of benzene was treated at room temp. with 1.20 g of Zn/Cu (2:1) and then stirred at 80 °C for 1 h. A change of colour from dark-brown to green occured. After cooling to 20 °C, the reaction mixture was filtered and 0.56 ml (2.95 mmol) of P*i*Pr$_3$ was added to the filtrate. The solution was heated under reflux for 30 min, and upon cooling to room temp. it was concentrated to ca. 3 ml in vacuo. Green crystals precipitated, the formation of which was enhanced by the addition of 5 ml of pentane. The mother liquor was decanted, the crystals were washed three times with 3 ml portions of pentane, and dried in vacuo; yield 386 mg (67%, m.p. 105 °C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1716 cm^{-1} [ν(NO)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.62 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, *N* = 13.6, *J*(HH) = 7.0 Hz, 36H, PCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 21.7 (vt, *N* = 23.1 Hz, P*C*HCH$_3$), 19.4 (s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 50.0 (s). – $C_{18}H_{42}ClNOP_2Ru$ (487.0): calcd. C 44.39, H 8.69, N 2.87; found C 44.28, H 8.49, N 2.92; mol. mass 487 (MS).

2. Preparation of trans-[RuCl(NO)(PiPr$_2$Ph)$_2$] (**3**): Compound **3** was prepared analogous to **2**, by using 491 mg (0.64 mmol) of **1**, 0.65 g of Zn/Cu (2:1) and 0.36 ml (1.92 mmol) of P*i*Pr$_2$Ph as starting materials; green, air-sensitive solid, yield 232 mg (65%), m.p. 104 °C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1720 cm^{-1} [ν(NO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.93–7.04 (m, 10H, C_6H_5), 2.96 (m, 4H, PC*H*CH$_3$), 1.46 [dvt, *N* = 15.7, *J*(HH) = 7.3 Hz, 12H, PCHC*H*$_3$], 1.27 [dvt, *N* = 13.6, *J*(HH) = 6.7 Hz, 12H, PCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 135.7, 133.9 (both vt, *N* = 11.2, *N* = 9.9 Hz, *o*-C and *m*-C of C_6H_5), 130.1 (s, *p*-C of C_6H_5), 129.0 (vt, *N* = 31.2 Hz, *ipso*-C of C_6H_5), 22.8 (vt, *N* = 22.5 Hz, P*C*HCH$_3$), 19.7, 18.1 (both s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 48.2 (s). – $C_{24}H_{38}ClNOP_2Ru$ (555.0): calcd. C 51.94, H 6.90, N 2.52, Ru 18.21; found C 52.10, H 6.61, N 2.32, Ru 18.12; mol. mass 555 (MS).

3. Preparation of [RuHCl$_2$(NO)(PiPr$_3$)$_2$] (**4**): A suspension of 135 mg (0.28 mmol) of **2** in 15 ml of benzene was treated dropwise with ether, which was saturated with HCl, at room temp. until a change of colour from green to orange had occured. An orange solid precipitated, the formation of which was encouraged by concentrating the solution to ca. 2 ml. The solid was filtered off, washed three times with 3 ml portions of ether, and dried in vacuo; yield 139 mg (96%), m.p. 93 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2058 cm^{-1} [ν(RuH)], 1790 [ν(NO)]. – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 2.73 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, *N* = 13.3, *J*(HH) = 6.6 Hz, 18H, PCHC*H*$_3$], 1.30 [dvt, *N* = 14.7, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$],

−4.58 [t, *J*(PH) = 16.2 Hz, 1 H, RuH]. – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 44.0 (s). – $C_{18}H_{43}Cl_2NOP_2Ru$ (523.5): calcd. C 41.30, H 8.28, N 2.67; found C 41.12, H 8.37, N 2.56.

4. Preparation of [RuHCl₂(NO)(PiPr₂Ph)₂] (**5**): Compound **5** was prepared analogous to **4**, by using 100 mg (0.18 mmol) of **3** and an etheral solution of HCl as starting materials; orange microcrystalline solid, yield 97 mg (91%), m.p. 92 °C (dec.). – IR (KBr): ṽ = 2077 cm^{-1} [ν(RuH)], 1816 [ν(NO)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 8.52–7.58 (m, 10 H, C_6H_5), 3.43 (m, 2 H, PC*H*CH$_3$), 3.09 (m, 2 H, PC*H*CH$_3$), 1.71 [dvt, *N* = 15.6, *J*(HH) = 7.3 Hz, 6 H, PCHC*H*$_3$], 1.56 [dvt, *N* = 15.9, *J*(HH) = 8.5 Hz, 6 H, PCHC*H*$_3$], 1.33 [dvt, *N* = 12.7, *J*(HH) = 6.6 Hz, 6 H, PCHC*H*$_3$], 1.23 [dvt, *N* = 13.8, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], −4.27 [t, *J*(PH) = 18.3 Hz, 1 H, RuH]. – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 38.9 (s). – $C_{24}H_{39}Cl_2NOP_2Ru$ (591.5): calcd. C 48.73, H 6.65, N 2.37; found C 48.41, H 6.44, N 2.30.

5. Preparation of [RuCl(NO)(CO)(PiPr₃)₂] (**6**): A slow stream of CO was passed through a solution of 155 mg (0.32 mmol) of **2** in 10 ml of benzene for 1 min at 5 °C. A change of colour from green to yellow occured. After the solution was concentrated to ca. 2 ml in vacuo, 5 ml of pentane was added. This led to the formation of a yellow-brownish solid that was separated from the mother liquor, washed twice with 5 ml portions of pentane and dried; yield 154 mg (94%), m.p. 98 °C (dec.). – IR (KBr): ṽ = 1913 cm^{-1} [ν(CO)], 1573 [ν(NO)]. – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 2.75 (m, 6 H, PC*H*CH$_3$), 1.20 [dvt, *N* = 13.4, *J*(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$], a second signal for the PCHC*H*$_3$ protons is partially covered by the signal at δ = 1.20. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 206.8 [t, *J*(PC) = 12.9 Hz, CO], 24.8 [vt, *N* = 21.6 Hz, PCHCH$_3$], 19.7, 19.0 (both s, PCH*C*H$_3$). – ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ = 48.8 (s). – $C_{19}H_{42}ClNO_2P_2Ru$ (515.0): calcd. C 44.31, H 8.22, N 2.72; found C 44.18, H 8.14, N 2.45.

6. Preparation of [RuCl(NO)(CO)(PiPr₂Ph)₂] (**7**): Compound **7** was prepared analogous to **6**, by using 211 mg (0.38 mmol) of **3** and CO as starting materials; yellow-brownish microcrystalline solid, yield 181 mg (90%), m.p. 96 °C (dec.). – IR (KBr): ṽ = 1912 cm^{-1} [ν(CO)], 1577 [ν(NO)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.74–7.03 (m, 10 H, C_6H_5), 3.51 (m, 2 H, PC*H*CH$_3$), 2.44 (m, 2 H, PC*H*CH$_3$), 1.26 [dvt, *N* = 15.4, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$], 1.03 [dvt, *N* = 15.0, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$], 0.88 [dvt, *N* = 16.1, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$], 0.80 [dvt, *N* = 14.6, *J*(HH) = 7.6 Hz, 6 H, PCHC*H*$_3$]. – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 44.7 (s). – $C_{25}H_{38}ClNO_2P_2Ru$ (583.1): calcd. C 51.50, H 6.57, N 2.40; found C 50.95, H 6.14, N 2.29.

7. Preparation of [RuCl(NO){κ²(C,C)-C₂(CN)₄}(PiPr₃)₂] (**8**): A solution of 155 mg (0.32 mmol) of **2** in 15 ml of toluene was treated with 41 mg (0.32 mmol) of tetracyanoethene and stirred for 2 h at room temp. While a change of colour from green to red-brown occured, a red-brown solid slowly precipitated, the formation of which was completed upon cooling to 0 °C. The solid was filtered off, washed twice with 5 ml portions of toluene and dried in vacuo; yield 174 mg (89%), m.p. 100 °C (dec.). – IR (CH$_2$Cl$_2$): ṽ = 2225 cm^{-1} [ν(CN)], 1808 [ν(NO)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 3.10 (m, 6 H, PC*H*CH$_3$), 1.44 [dvt, *N* = 15.4, *J*(HH) = 7.6 Hz, 18 H, PCHC*H*$_3$], 1.37 [dvt, *N* = 15.0, *J*(HH) = 7.5 Hz, 18 H, PCHC*H*$_3$]. – ^{13}C-NMR (C_6D_6, 50.3 MHz): δ = 114.0 [t, *J*(PC) = 1.8 Hz, CN], 47.1 [t, *J*(PC) = 4.3 Hz, =*C*(CN$_2$)], 28.6 (vt, *N* = 18.3 Hz, P*C*HCH$_3$), 20.1, 19.7 (both s, PCH*C*H$_3$). – ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ = 34.9 (s). – $C_{24}H_{42}ClN_5OP_2Ru$ (615.1): calcd. C 46.87, H 6.88, N 11.38; found C 46.53, H 7.14, N 11.22.

8. Preparation of [RuCl(NO){κ²(C,C)-C₂(CN)₄}(PiPr₂Ph)₂] (**9**): Compound **9** was prepared analogous to **8**, by using 205 mg (0.37 mmol) of **3** and 47 mg (0.37 mmol) of tetracyanoethene as starting materials; red-brown microcrystalline solid, yield 202 mg (80%), m.p. 102 °C (dec.). – IR (CH$_2$Cl$_2$): ṽ = 2227 cm^{-1} [ν(CN)], 1818 [ν(NO)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.62–7.47 (m, 10 H, C_6H_5), 3.16 (m, 2 H, PC*H*CH$_3$), 2.94 (m, 2 H, PC*H*CH$_3$), 1.52 [dvt, *N* = 15.4, *J*(HH) = 7.3 Hz, 6 H, PCHC*H*$_3$], 1.46 [dvt, *N* = 14.3, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$], 1.42 [dvt, *N* = 14.1, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$], a further signal for the PCHC*H*$_3$ protons is partially covered by the signal at δ = 1.46. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 133.3, 129.4 (both vt, *N* = 5.9 and 8.8 Hz, *o*-C and *m*-C of C_6H_5), 131.8 (s, *p*-C of C_6H_5), 114.6 [t, *J*(PC) = 1.9 Hz, CN], 48.1 [t, *J*(PC) = 4.9 Hz, =*C*(CN$_2$)], 29.6 (vt, *N* = 17.7 Hz, P*C*HCH$_3$), 28.9 (vt, *N* = 16.8 Hz, P*C*HCH$_3$), 21.2, 20.8, 20.1, 19.8 (all s, PCH*C*H$_3$), signal for *ipso*-C of C_6H_5 covered by solvent signal. – ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ = 36.0 (s). – $C_{30}H_{38}ClN_5OP_2Ru$ (683.1): calcd. C 52.75, H 5.61, N 10.25, Ru 14.80; found C 53.21, H 5.33, N 10.68, Ru 14.13.

9. Preparation of [RuCl(NO)(=CH₂)(PiPr₂Ph)₂] (**10**): A solution of 163 mg (0.29 mmol) of **3** in 10 ml of toluene was treated at 0 °C dropwise with a solution of CH$_2$N$_2$ in ether until a change of colour from green to off-white had occured. During the reaction, an intense gas evolution took place. The solvent was removed, the residue was extracted with 2 ml of benzene, and the extract was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 4 cm). With benzene, an off-white fraction was eluted which was evaporated to dryness in vacuo. The residue was dissolved in 3 ml of CH$_2$Cl$_2$/EtOH (1:1), and the solution was slowly evaporated until a precipitate was formed. After storing for 12 h at −78 °C, the off-white microcrystalline solid was filtered off, washed with pentane and dried; yield 87 mg (52%), m.p. 92 °C (dec.). – IR (KBr): ṽ = 1610 cm^{-1} [ν(NO)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 13.71 [t, *J*(PH) = 15.8 Hz, 2 H, Ru=CH$_2$], 7.89–7.01 (m, 10 H, C_6H_5), 2.87 (m, 2 H, PC*H*CH$_3$), 2.52 (m, 2 H, PC*H*CH$_3$), 1.32 [dvt, *N* = 14.5, *J*(HH) = 7.2 Hz, 6 H, PCHC*H*$_3$], 1.29 [dvt, *N* = 14.3, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], 0.91 [dvt, *N* = 15.1, *J*(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$], 0.81 [dvt, *N* = 13.8, *J*(HH) = 6.3 Hz, 6 H, PCHC*H*$_3$]. – ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 205.4 [t, *J*(PC) = 12.1 Hz, Ru=CH$_2$], 134.7, 129.2 (both vt, *N* = 8.4 and 9.8 Hz, *o*-C and *m*-C of C_6H_5), 131.0 (s, *p*-C of C_6H_5), 128.0 (vt, *N* = 41.2 Hz, *ipso*-C of C_6H_5), 24.9 (vt, *N* = 30.8 Hz, P*C*HCH$_3$), 24.2 (vt, *N* = 28.6 Hz, P*C*HCH$_3$), 20.1, 19.3, 19.2, 18.4 (all s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 47.0 (s). – $C_{25}H_{40}ClNOP_2Ru$ (569.1): calcd. C 52.77, H 7.09, N 2.46; found C 52.38, H 6.84, N 2.31.

10. Preparation of [RuCl(NO)(η²-O₂)(PiPr₃)₂] (**11**): A slow stream of oxygen was passed through a solution of 142 mg (0.29 mmol) of **2** in 15 ml of benzene for 2 min at room temp. A smooth change of colour from green to brown occured. The solvent was removed, the oily residue was treated with 10 ml of pentane, and the mixture was irradiated for 10 min in an ultrasonic bath. A brown solid was formed that was filtered off, washed twice with 3 ml portions of pentane and dried in vacuo; yield 123 mg (81%), m.p. 100 °C (dec.). – IR (KBr): ṽ = 1752 cm^{-1} [ν(NO)], 870 [ν(O$_2$)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.93 (m, 6 H, PC*H*CH$_3$), 1.47 [dvt, *N* = 14.4, *J*(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$], 1.36 [dvt, *N* = 15.1, *J*(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$]. – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 27.8 (s). – $C_{18}H_{42}ClNO_3P_2Ru$ (519.1): calcd. C 41.65, H 8.16, N 2.70; found C 41.52, H 8.04, N 2.34.

11. Preparation of [RuCl(NO)(η²-O₂)(PiPr₂Ph)₂] (**12**): Compound **12** was prepared analogous to **11**, by using 180 mg (0.32

mmol) of **3** and oxygen as starting materials; brown microcrystalline solid; yield 145 mg (76%); m.p. 102 °C (dec.). – IR (KBr): ṽ = 1756 cm^{-1} [ν(NO)], 866 [ν(O$_2$)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 8.02–7.58 (m, 10H, C$_6$H$_5$), 3.15 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 2.94 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.56 [dvt, *N* = 14.3, *J*(HH) = 6.9 Hz, 6H, $\mathrm{PCHC}H_3$], 1.46 [dvt, *N* = 15.7, *J*(HH) = 7.7 Hz, 6H, $\mathrm{PCHC}H_3$], 1.42 [dvt, *N* = 15.4, *J*(HH) = 7.9 Hz, 6H, $\mathrm{PCHC}H_3$], a further signal for the $\mathrm{PCHC}H_3$ protons is partially covered by the signal at δ = 1.46. – ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ = 28.3 (s). – $\mathrm{C_{24}H_{38}ClNO_3P_2Ru}$ (587.0): calcd. C 49.10, H 6.52, N 2.38; found C 48.57, H 6.68, N 2.24.

12. Preparation of [RuCl(NO){η^2(O,O)-O$_2$SO$_2$}(PiPr$_3$)$_2$] (**13**): A slow stream of SO$_2$ was passed through a solution of 102 mg (0.20 mmol) of **11** in 10 ml of toluene for 2 min at room temp. A slight change of colour from brown to orange-brown occured. The solvent was removed, the residue was dissolved in 2 ml of toluene, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 4 cm). With toluene, an orange fraction was eluted, which was brought to dryness in vacuo. The residue was dissolved in 2 ml of toluene/pentane (1:5), and the solution was slowly evaporated until a precipitate was formed. Upon cooling to −60 °C, an orange microcrystalline solid was obtained that was filtered, washed twice with pentane and dried; yield 71 mg (62%), m.p. 142 °C (dec.). – IR (KBr): ṽ = 1816 cm^{-1} [ν(NO)], 1284, 1156, 885, 863, 661 [ν(SO)]. – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.26 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$), 1.34 [dvt, *N* = 14.8, *J*(HH) = 7.2 Hz, 18H, $\mathrm{PCHC}H_3$], 1.28 [dvt, *N* = 13.9, *J*(HH) = 7.0 Hz, 18H, $\mathrm{PCHC}H_3$]. – ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ = 41.3 (s). – $\mathrm{C_{18}H_{42}ClNO_5P_2RuS}$ (583.1): calcd. C 37.08, H 7.26, N 2.40, S 5.49; found C 37.19, H 7.37, N 2.51, S 5.39.

13. Preparation of [RuCl(NO){η^2(O,O)-O$_2$SO$_2$}(PiPr$_2$Ph)$_2$] (**14**): Compound **14** was prepared analogous to **13**, by using 117 mg (0.20 mmol) of **12** and SO$_2$ as starting materials; orange microcrystalline solid, yield 78 mg (60%), m.p. 139 °C (dec.). – IR (KBr): ṽ = 1819 cm^{-1} [ν(NO)], 1282, 1159, 882, 861, 660 [ν(SO)]. – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.67–7.33 (m, 10H, C$_6$H$_5$), 3.53 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 3.26 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.46 [dvt, *N* = 14.2, *J*(HH) = 6.9 Hz, 6H, $\mathrm{PCHC}H_3$], 1.29 [dvt, *N* = 14.6, *J*(HH) = 7.2 Hz, 6H, $\mathrm{PCHC}H_3$], 1.22 [dvt, *N* = 14.4, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$], a further signal for the $\mathrm{PCHC}H_3$ protons is partially covered by the signal at δ = 1.29. – ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ = 40.0 (s). – $\mathrm{C_{24}H_{38}ClNO_5P_2RuS}$ (651.1): calcd.C 44.27, H 5.88, N 2.15, S 4.91; found C 44.13, H 5.41, N 1.88, S 4.42.

14. Determination of the X-ray Crystal Structure of **2**[28]: Single crystals were grown from pentane/benzene (4:1) at −18 °C. Crystal data (from 25 reflections, 10° < Θ < 15°): monoclinic, space group *P*2$_1$/*c* (No. 14); *a* = 8.127(7) Å, *b* = 8.964(3) Å, *c* = 16.66(1) Å, β = 93.02(4), *V* = 1212(1) Å^3, *Z* = 2, d_{calcd} = 1.33 g cm^{-3}, μ(Mo-K_α) = 1.76 mm^{-1}; crystal size 0.1 × 0.15 × 0.45 mm; Enraf-Nonius CAD4 diffractometer, Mo-K$_\alpha$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4); *T* = 293 K; ω/Θ scan, max 2Θ = 52°; 2704 reflections measured, 2340 independent reflections, 1913 reflections with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ-scan method) was applied (minimum transmission 95.81%). The structure was solved by direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (738 parameters, unit weights, SDP). The positions of all hydrogen atoms were found and refined isotropically. *R* = 0.020 and *wR* = 0.021; reflex/parameter ratio 9.07; residual electron density +0.45/−0.38 eÅ^{-3}.

15. Determination of the X-ray Crystal Structure of **13**[28]: Single crystals were grown from benzene. Crystal data (from 25 reflections, 10° < Θ < 20°): orthorhombic, space group *Pca*2$_1$ (No. 29); *a* = 15.411(2) Å, *b* = 11.856(2) Å, *c* = 14.565(2) Å, *V* = 2661.2(7) Å^3, *Z* = 4, d_{calcd} = 1.455 g cm^{-3}, μ(Mo-*K*α) = 0.906 mm^{-1}; crystal size 0.15 × 0.20 × 0.35 mm; Enraf-Nonius CAD4 diffractometer, Mo-*K*α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4); *T* = 293 K; ω/Θ scan, max. 2Θ = 64°; 4493 reflections measured, 4170 independent reflections, 2922 reflections with $I > 2\sigma(I)$, all 4170 independent reflections included in data set. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares on F^2 (274 parameters, weighting scheme applied in the last cycle: $w = 1/[\sigma^2(F_o^2) + (0.0382{*}P)^2 + 0.6745{*}P]$ where $P = (F_o^2 + 2F_c^2)/3$, SHELXL-93). The positions of all hydrogen atoms were calculated according to ideal geometry and were refined using the riding method. Conventional *R* = 0.0357 [for 2922 reflections with $I > 2\sigma(I)$] and weighted *wR*2 = 0.0886 for all 4170 data reflections; reflex/parameter ratio 19.2; residual electron density +0.689−0.386 eÅ^{-3}. Attempts to solve the structure of **13** in the alternative space group *Pbcm* (No. 57) were unsuccessful.

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