Two Alternatives of Heteroallene Insertion in Metal–Ligand Bonds of Five-Coordinate Ruthenium(II) and Osmium(II) Complexes [MXY(CO)(P*i*Pr$_3$)$_2$]☆

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Received September 2, 1994

Key Words: Ruthenium complexes / Osmium complexes / Insertion reactions / Carbon disulfide / Carbon dioxide / Methyl isothiocyanate / Zwitterionic ligands

The five-coordinate chloro(hydrido)- and hydrido(iodo)ruthenium(II) and -osmium(II) compounds [MHX(CO)(P*i*Pr$_3$)$_2$] (**1**, **2**, **6**, **7**) react with CS_2 to give the octahedral dithioformato complexes [MCl(CO)(P*i*Pr$_3$)$_2$(η^2-S_2CH)] (**3**, **4**, **8**, **9**) in excellent yields. In the initial step, an addition of the heteroallene to the metal center occurs which is followed by insertion of CS_2 into the M–H bond. On treatment of the dichlororuthenium(II) derivative [$RuCl_2$(CO)(P*i*Pr$_3$)$_2$] (**10**), which is prepared from $RuCl_3$ · aq and P*i*Pr$_3$ in methanol, with carbon disulfide insertion into one of the Ru–P*i*Pr$_3$ bonds takes place to give the six-coordinate ruthenium(II) complex **12** with the zwitterion ^-S_2CP*i*Pr$_3^+$ as a chelating ligand. While the reaction of [OsH(SPh)(CO)(P*i*Pr$_3$)$_2$] (**13**) with MeSCN leads to addition of the thionitrile to the metal center, the starting material reacts with MeNCS by insertion of the heteroallene into the Os–SPh bond to give two stereoisomers **15a**, **b**, in which the nitrogen atom of the chelate ring is either *cis* or *trans* to the hydrido ligand. The octahedral methoxydithiocarbonato- and formatoosmium(II) compounds **16** and **17** are prepared from **2** and CS_2 or CO_2 in the presence of NaOMe. The crystal and molecular structures of **4** (M = Os), **12** and **15a** have been determined.

We have recently shown that the coordinatively unsaturated chloro(hydrido)ruthenium(II) and -osmium(II) compounds [MHCl(CO)(P*i*Pr$_3$)$_2$] (**1**, **2**) react with small molecules L such as H_2, O_2, CO, CNR and CH_2=CHX to form octahedral complexes [MHCl(CO)(P*i*Pr$_3$)$_2$L] in which the new ligand L occupies the free coordination site[1,2]. If the starting materials **1**, **2** are transformed into the corresponding hydrido(phenolato)- and hydrido(thiophenolato)metal derivatives [MH(EC_6X_5)(CO)(P*i*Pr$_3$)$_2$] (E = O, S; X = H, F), we have observed that these compounds on treatment with CS_2 undergo insertion reactions to yield the chelate complexes [MH(η^2-S_2COC_6X_5)(CO)(P*i*Pr$_3$)$_2$] and [MH(η^2-S_2CSC_6X_5)(CO)(P*i*Pr$_3$)$_2$], respectively[3]. Since terminal alkynes insert into the M–H bond of **1** and **2**[4], we were interested to know whether a similar process could occur with heteroallenes such as CS_2, SCNR, OCNR and even with CO_2. In this paper we describe the synthesis of dithioformato-, dithiocarbamato-, dithiocarbonato-, and formatoruthenium and -osmium compounds which are all formed by heteroallene insertion. We furthermore report that in the absence of a hydrido or thiophenolato ligand, a five-coordinate d^6 metal complex of general composition [MX_2(CO)(PR_3)$_2$] can equally undergo a CS_2 insertion, in this case however, not into the M–X but into one of the M–PR_3 bonds.

Results

Insertion of CS_2 into Ru–H and Os–H Bonds

The chloro(hydrido) complexes **1** and **2** react with an excess of CS_2 in dichloromethane at room temperature to give the insertion products **3** and **4** (Scheme 1) in almost quantitative yields. Both compounds are red air-stable solids which with the exception of pentane and hexane are readily soluble in all common organic solvents. The presence of a dithioformate ligand is illustrated by the appearance of a triplet in the ^{13}C-NMR spectrum at δ = 226.9 (**3**) and 221.1 (**4**) for the S_2C*H* carbon atom and by a low-field ^{1}H-NMR signal at δ = 10.5 (**3**) and 12.1 (**4**) for the S_2C*H* proton which due to a long-range P-H coupling is also split into a triplet. With regard to the mechanism of formation of compounds **3** and **4**, it is in general conceivable that initially a coordination of the heteroallene to the metal center occurs which is followed by the insertion (or hydride migration) step. At least for M = Os, this proposal has been substantiated by the isolation of the 1:1 adduct **5** which is obtained in the reaction of **2** with CS_2 if instead of CH_2Cl_2 acetone is used as the solvent. The ^{1}H-NMR spectrum of the yellow solid displays a triplet at δ = –2.85 for the OsH proton, the position of which is indicative of the coordination of a strong π-acceptor ligand *trans* to the hydrido ligand. Although due to the facile rearrangement of **5** to **4** a ^{13}C-NMR spectrum of the pure adduct **5** could not be recorded, the single ^{31}P-NMR resonance signal confirms that the two phosphane ligands are equivalent.

The hydrido(iodo)ruthenium(II) and -osmium(II) derivatives **6** and **7**, which are prepared from **1** and **2** by metathetical exchange with LiI, behave similarly and also react quite smoothly with CS_2 to yield the dithioformato complexes **8** and **9**. In this case, however, we failed to isolate an

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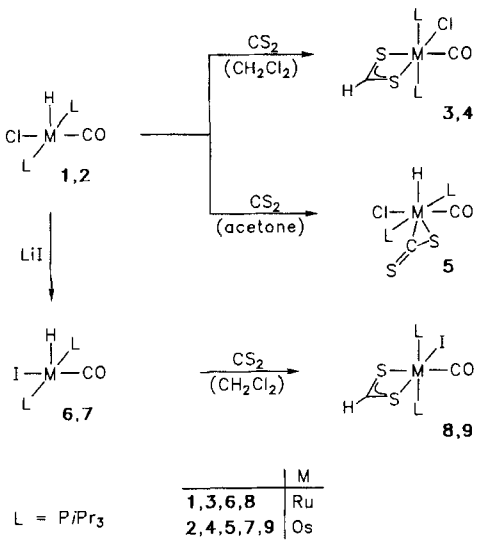
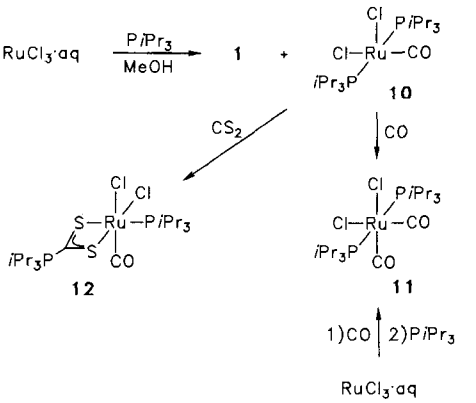
Scheme 1



Scheme 2



$M-CS_2$ adduct which suggests that the addition (and not the insertion) is the rate-determining step. We know already from our previous work on the reactivity of phosphanepalladium compounds toward CS_2 and CSe_2 that the type of anionic ligands sometimes significantly influences the rate of the heteroallene insertion[5]. In addition, Caulton et al. have reported more recently that the group X of the complexes $[RuHX(CO)(PMe\textit{t}Bu_2)_2]$ has a profound influence on the reactivity toward D_2, MeC≡CMe and PhC≡CH[6]. In this case the hydrido(iodo) compound is more reactive than the chloro(hydrido) derivative which on the basis of *ab initio SCF* calculations is explained by the more favorable opening of the H–Ru–I compared with the H–Ru–Cl angle[6]. We finally note that the spectroscopic data of **3**, **4** on one hand and of **8**, **9** on the other hand show only marginal differences and thus the arrangement of the ligands around the metal center should be the same.

An Unexpected Insertion Reaction: Preparation and Molecular Structure of $[RuCl_2(CO)(PiPr_3)(\eta^2\text{-}S_2CPiPr_3)]$ (12)

During attempts to optimize the synthesis of **1**, we have found that if the phosphane is added dropwise to a suspension of $RuCl_3 \cdot aq$ in methanol at 60°C instead of room temperature and the reaction mixture then heated for 24 h under reflux, a second minor product is formed besides the chloro(hydrido)ruthenium(II) derivative. Both the elemental analysis and the spectroscopic data confirm that this is the formerly unknown dichloro complex **10** (Scheme 2). Since we know that $[RuCl_2(CO)(PCy_3)_2]$[7] as well as the related five-coordinate osmium compound [OsCl(CH=CHPh)(CO)$(PiPr_3)_2$][4a] possess a square-pyramidal geometry, we assume that **10** has an analogous configuration.

On treatment with carbon monoxide, **10** reacts spontaneously by filling the free coordination site to give the dicarbonyl complex **11** in more than 80% yield. The same compound is obtained quantitatively if a solution of $RuCl_3 \cdot aq$ in 2-methoxyethanol is first stirred at 80°C under CO and then treated with triisopropylphosphane. The IR spectrum of **11** which forms yellow air-stable crystals displays only one CO stretching band and the ^{31}P-NMR spectrum equally only one resonance signal, and therefore an *all,trans* configuration of the octahedral molecule can be assumed.

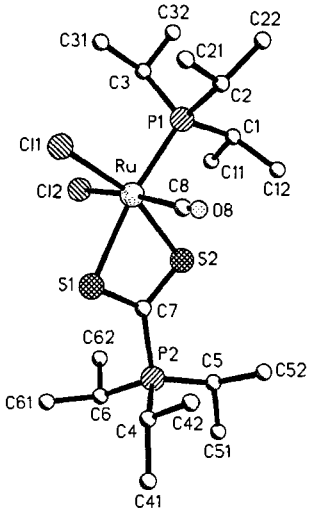
The reaction of **10** with CS_2 in chloroform is much slower than that with CO and affords after two days at room temperature a dark crystalline product which is analyzed as **10** · CS_2. Both the ^1H- and the ^{31}P-NMR spectra reveal, however, that the new compound **12** is not a 1:1 adduct like **11** but instead a complex containing two distinctly different $PiPr_3$ units. The ^{13}C-NMR spectrum displays in the low-field region besides the signal for the metal-bonded CO at $\delta = 195.75$ a second doublet at $\delta = 224.15$ which can be assigned to the carbon atom of a zwitterionic $^-S_2CPiPr_3^+$ ligand[8]. Thus, the conclusion is that on treatment of **10** with CS_2 an insertion of the heteroallene into one of the $Ru-PiPr_3$ bonds occurs.

The structural proposal for **12** shown in Scheme 2 has been confirmed by an X-ray crystal-structure investigation. The SCHAKAL diagram (Figure 1) reveals that the geometry around the ruthenium(II) center is distorted octahedrally. The smallest corner-to-center-to-corner angle S1–Ru–S2 is 71.4(1)° which is due to the unequal interatomic distances within the [Ru,S1,S2,C7] plane. The two Ru–S bond lengths are also significantly different [2.477(1) and 2.349(1) Å] which we attribute to the different *trans*-directing influence of the *trans*-disposed phosphane and chlorine ligands. The Cl2–Ru–C8 unit is almost linear [174.9(3)°] whereas the S1–Ru–P1 and even more so the S2–Ru–Cl1 axes are slightly bent. The Ru–Cl distances are in the expected range[9] and the Ru–P1 bond length is nearly identical with those in $[Ru(\eta^2\text{-}S_2CH)_2(PPh_3)_2]$[10].

Addition and Insertion Reactions of the Thiophenolato Complex 13

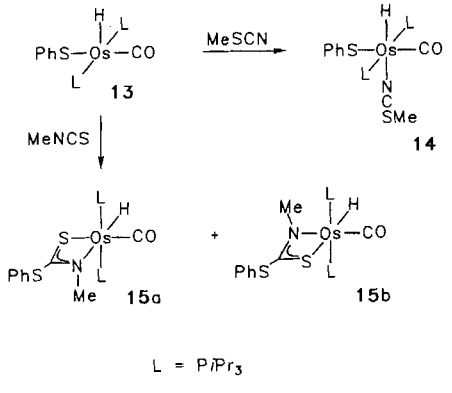
The thiophenolato complex **13** which is easily accessible from **2** and NaSPh not only reacts with CS_2[3] but also with MeSCN and the isomer MeNCS (Scheme 3). Whereas with the thioisocyanate a simple addition occurs to give the six-coordinate hydridoosmium(II) derivative **14**, the heteroallene undergoes an insertion into the Os–SPh but not, as in

Figure 1. Molecular structure of **12**; selected bond lengths [Å] and angles [°]: Ru–Cl1 2.423(1), Ru–Cl2 2.451(1), Ru–S1 2.477(1), Ru–S2 2.349(1), Ru–P1 2.355(1), S1–C7 1.667(4), S2–C7 1.670(4), P2–C7 1.815(4), P1–C1 1.855(4), P1–C2 1.851(3), P1–C3 1.861(4), P2–C4 1.826(4), P2–C5 1.819(4), P2–C6 1.823(3); Cl1–Ru–Cl2 91.0(1), Cl1–Ru–S1 91.7(1), Cl1–Ru–S2 163.1(1), Cl1–Ru–C8 91.6(2), Cl1–Ru–P1 97.4(1), Cl2–Ru–S1 90.2(1), Cl2–Ru–S2 88.0(1), Cl2–Ru–C8 174.9(3), Cl2–Ru–P1 91.6(1), P1–Ru–S1 170.6(1), P1–Ru–S2 99.5(1), P1–Ru–C8 92.4(2), C8–Ru–S1 85.3(2), C8–Ru–S2 88.3(2), S1–Ru–S2 71.4(1), Ru–C8–O8 173.2(13), Ru–S1–C7 84.6(1), Ru–S2–C7 88.8(1), S1–C7–S2 115.2(2), S1–C7–P2 122.6(2), S2–C7–P2 122.2(2)



the case of **2**, into the Os–H bond. Compound **14** is a white air-sensitive solid which has been characterized both by elemental analysis and by IR and NMR spectroscopy.

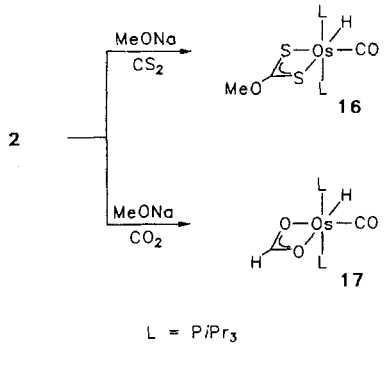
Scheme 3



The reaction of **13** with methyl isothiocyanate yields, depending on the reaction conditions, either one or two products. If a benzene solution of the two substrates is stirred at 25°C for 15 min, a single compound is obtained which due to the X-ray crystal-structure analysis is the isomer **15a** (Scheme 3). Extending the reaction time to about 10 h yields, however, a light yellow air-stable solid which undoubtedly is a mixture of two isomers. The ^{1}H-NMR spectrum displays two high-field signals at $\delta = -15.0$ and -15.4 in the intensity ratio of 2:3, whereas in the ^{13}C-NMR spectrum two triplets at $\delta = 182.5$ and 175.8 assigned to an sp^2-hybridized NCS_2 carbon atom appear. The obvious conclusion is that the kinetically preferred insertion product is compound **15a** containing the NMe unit of the chelate ligand *trans* to the hydrido ligand, and that after several hours an equilibrium mixture is formed in which both isomers are present in comparable quantities. We failed to separate the isomeric mixture by chromatographic techniques and also to prepare a pure sample of **15b** either by heating or photolysis of the reaction mixture. It should be mentioned that Robinson et al. have described the synthesis of various (*N*-alkyl- and *N*-arylthioformamido)metal complexes by insertion of SCNR (R = Me, Et, Ph, *p*-Tol) into an M–H bond of hydridoruthenium(II), -osmium(II) and -iridium(III) compounds, and that in the reaction of $[OsHCl(CO)(PPh_3)_3]$ with methyl and ethyl isothiocyanate the formation of an isomeric mixture has also been observed[11]. Attempts to separate this mixture and unequivocally characterize the isomers have remained unsuccessful[11].

An insertion process similar to that occurring in the formation of **15a,b** probably also takes place on treatment of a solution of **2**/NaOMe in benzene/methanol with CS_2 (Scheme 4). In agreement with the behavior of **2** toward $NaOC_6H_5$[3], we assume that initially a hydrido(methoxy)osmium intermediate is generated which reacts with the heteroallene to give the *O*-methyldithiocarbonato complex **16**. The presence of the OCH_3 substituent at the chelate ring is indicated by a ^{1}H-NMR signal at $\delta = 3.6$ and by a corresponding resonance signal in the ^{13}C-NMR spectrum at $\delta = 54.8$. The equivalence of the phosphane ligands is confirmed by the appearance of one singlet in the ^{31}P-NMR spectrum which in off-resonance is split into a doublet due to P–H coupling.

Scheme 4



If under the same conditions which are used for the preparation of **16**, the solution of **2** and NaOMe in benzene/methanol is treated with CO_2, instead of a compound with a chelating monoanionic O_2COMe ligand the formato complex **17** is formed. The isolated yield of the white crystalline solid is 82%. Since the starting material **2** is completely inert toward CO_2, we assume that in the initial step of the reaction an intermediate $[OsH(OCH_3)(CO)(PiPr_3)_2]$ is generated which by elimination of CH_2O gives $[OsH_2(CO)(PiPr_3)_2]$. It is probably this compound which reacts with CO_2 to yield **17**. To explain the different behavior of the supposed intermediates toward CS_2 and CO_2, we note that there is ample precedent in the literature indicating that the

insertion of CO_2 into an M–H bond occurs much more readily than that of CS_2[12]. Characteristic spectroscopic features of complex **17**, which can also be prepared by ligand exchange from **2** and HCO_2Na, are the ^{1}H-NMR signal for the HCO_2 proton at $\delta = 8.8$, the hydrido resonance signal at $\delta = -21.2$, and the low-field singlet for the HCO_2 carbon atom in the ^{13}C-NMR spectrum at $\delta = 173.5$. We finally note that the formation of the dihydrido complex $[OsH_2(CO)(PiPr_3)_2]$ as an intermediate has already been implicated in our mechanistic studies of the hydrogen transfer from 2-propanol to cyclohexanone, acetophenone, benzylidenacetone and phenylacetylene catalyzed by **2**[2b,13]. It is also thought to play a key role in the reactions of $[OsH(\eta^2\text{-}H_2BH_2)(CO)(PiPr_3)_2]$ with nucleophiles[14].

X-ray Structural Analyses of Compounds 4 and 15a

The molecular structures of the two osmium complexes **4** and **15a** which are formed by insertion of heteroallenes into Os–H and Os–SPh bonds are shown in Figures 2 and 3. In both molecules the metal center is octahedrally coordinated with the two phosphane ligands in *trans* position. The bending of the P–Os–P axis is more pronounced in the dithiocarbamato compound **15a** which could be due to steric hindrance between the substituents at the OsNCS four-membered ring and the isopropyl groups of the phosphane ligands. In agreement with the structural data of **12**, also in complex **4** the two metal–sulfur bond lengths are distinctly different [2.356(1) and 2.497(1) Å], the longer distance being opposite to the stronger *trans*-directing CO ligand. The influence of the two unequal chelate rings on the structural parameters is illustrated by the difference in the Os–P bond lengths which are 2.433(1) and 2.447(1) Å for **4**, but only 2.328(1) and 2.338(1) Å for **15a**. The carbon–sulfur distances in **4** lie in between those of a C–S single and double bond and are almost identical with those of other octahedral (dithioformato)metal complexes[10,15]. In **15a**, the bond length S1–C2 is somewhat shorter [1.702(3) Å] than that between the ring carbon and the exocyclic sulfur atom [1.774(3) Å], which reflects the charge delocalization in the chelate ring. This conclusion is consistent with the N1–C2 distance [1.267(4) Å] which is only slightly longer than that of a C=N bond[16]. Although the position of the metal-bonded hydrogen atom of **15a** could not be exactly determined, according to the bond angles P1–Os–C3, P2–Os–C3 and S1–Os–C3 there is no doubt that it occupies the sixth coordination site.

Figure 2. Molecular structure of **4**; selected bond lengths [Å] and angles [°]: Os–Cl 2.432(1), Os–S1 2.356(1), Os–S2 2.497(1), Os–P1 2.433(1), Os–P2 2.447(1), Os–C2 1.877(5), S1–C1 1.665(7), S2–C1 1.671(6), C2–O 1.087(7); P1–Os–P2 169.10(5), P1–Os–Cl 84.41(5), P1–Os–C2 89.3(2), P1–Os–S1 95.04(5), P1–Os–S2 91.08(5), P2–Os–Cl 87.85(5), P2–Os–C2 85.1(2), P2–Os–S1 94.80(5), P2–Os–S2 96.70(5), Cl–Os–C2 104.0(1), Cl–Os–S1 160.73(5), Cl–Os–S2 90.91(5), S1–Os–S2 69.83(5), S1–Os–C2 95.3(2), S2–Os–C2 165.1(2), Os–S1–C1 91.1(2), Os–S2–C1 86.1(2), S1–C1–S2 112.9(3), Os–C2–O 175.7(5)

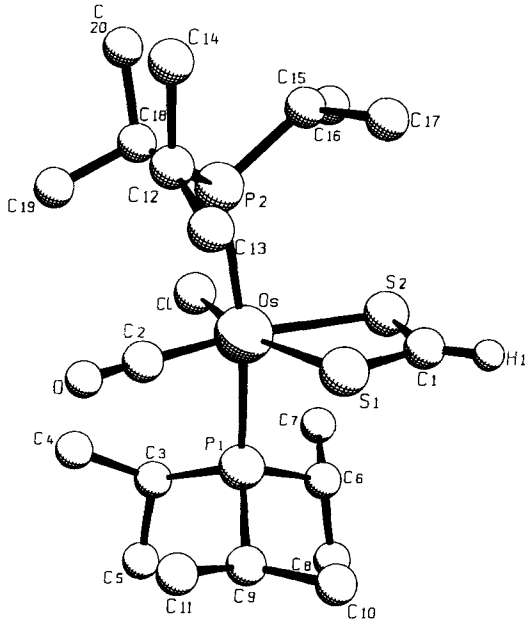
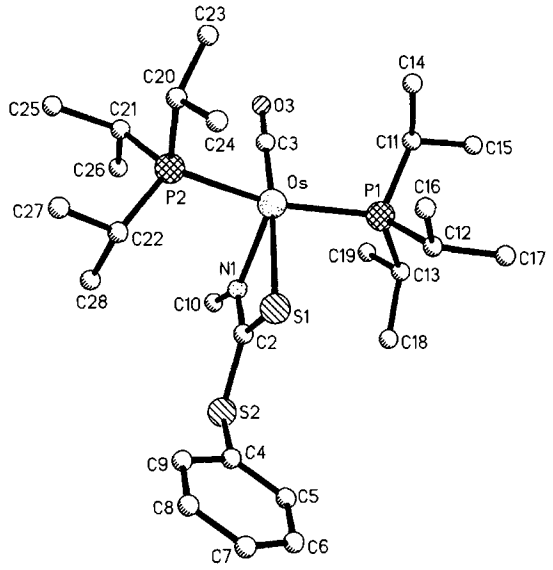


Figure 3. Molecular structure of **15a**; selected bond lengths [Å] and angles [°]: Os–P1 2.328(1), Os–P2 2.338(1), Os–S1 2.481(1), Os–N1 2.201(2), Os–C3 1.780(3), N1–C2 1.267(4), N1–C10 1.437(5), S1–C2 1.702(3), S2–C2 1.774(3), S2–C4 1.718(4), C3–O3 1.141(4); P1–Os–P2 163.3(1), P1–Os–N1 99.9(1), P1–Os–S1 88.3(1), P1–Os–C3 92.8(1), P2–Os–N1 96.2(1), P2–Os–S1 95.0(1), P2–Os–C3 86.7(1), N1–Os–S1 63.8(1), N1–Os–C3 106.2(1), S1–Os–C3 170.0(1), Os–N1–C2 102.6(2), Os–N1–C10 137.6(2), Os–S1–C2 80.6(1), C2–N1–C10 119.8(2), N1–C2–S1 113.0(2), S1–C2–S2 126.2(2), N1–C2–S2 120.9(2), C2–S2–C4 102.9(2), Os–C3–O3 179.3(2)



This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We also thank the *Degussa AG* for generous gifts of chemicals, Mrs. *U. Neumann*, Mrs. *R. Schedl* and Mr. *C. P. Kneis* for elemental analyses and DTA measurements, and Dr. *G. Lange* and Mr. *F. Dadrich* for recording the mass spectra.

Experimental

All operations were carried out under Ar with the Schlenk-tube technique. The starting materials **1**, **2**[1] and **13**[3] were prepared by published procedures. – IR: Perkin-Elmer 1420. – NMR: Jeol FX

90 Q, Bruker AC 200 and AMX 400; vt = virtual triplet. – MS: Varian MAT CH7.

1. *Preparation of [RuCl(CO)(PiPr$_3$)$_2$(η^2-S$_2$CH)]* (**3**): A solution of 92 mg (0.19 mmol) of **1** in 5 ml of dichloromethane was treated with 0.1 ml (1.7 mmol) of CS_2 and stirred for 1 h at room temp. The solution was concentrated until a precipitate appeared, and then stored at −78°C for 6 h. Deep red crystals formed which were repeatedly washed with methanol (−30°C) and dried in vacuo; yield 99 mg (92%). – IR (KBr): $\tilde{\nu}$ = 1930 cm^{-1} [ν(CO)], 919 [ν(CS)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 10.51 [t, *J*(PH) = 3.7 Hz, 1H, S_2CH], 2.60 (m, 6H, PC*H*CH$_3$), 1.39 [dvt, *N* = 14.0, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$], 1.18 [dvt, *N* = 12.6, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 226.95 [t, *J*(PC) = 5.5 Hz, S_2CH], 207.85 [t, *J*(PC) = 12.9 Hz, CO], 25.87 (vt, *N* = 20.3 Hz, P*C*HCH$_3$), 21.03, 20.27 (both s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162 MHz): δ = 36.44 (s). – $C_{20}H_{43}ClOP_2RuS_2$ (562.3): calcd. C 42.72, H 7.72; found C 42.76, H 7.75; mol. mass 562 (MS).

2. *Preparation of [OsCl(CO)(PiPr$_3$)$_2$(η^2-S$_2$CH)]* (**4**): Analogously as described for **3**, by using 110 mg (0.19 mmol) of **2** as starting material; deep red crystals; yield 113 mg (91%); m.p. 175°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1908 cm^{-1} [ν(CO)], 916 [ν(CS)]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 12.15 [t, *J*(PH) = 2.8 Hz, 1H, S_2CH], 2.82 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, *N* = 14.0, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.31 [dvt, *N* = 12.4, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 221.06 (s, S_2CH), 183.39 [t, *J*(PC) = 9.4 Hz, CO], 25.40 (vt, *N* = 25.2 Hz, P*C*HCH$_3$), 20.66, 20.03 (both s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 1.71 (s). – $C_{20}H_{43}ClOOsP_2S_2$ (651.4): calcd. C 36.88, H 6.66; found C 37.02, H 6.80; mol. mass 652 (MS).

3. *Preparation of [OsHCl(CO)(CS$_2$)(PiPr$_3$)$_2$]* (**5**): A solution of 120 mg (0.21 mmol) of **2** in 10 ml of acetone was treated with 0.5 ml of CS_2 and stirred for 5 min at room temp. The solvent was removed, the yellow solid was repeatedly washed with methanol (−30°C) and dried in vacuo; yield 117 mg (86%). – IR (KBr): $\tilde{\nu}$ = 1935 cm^{-1} [ν(CO)]. – ^{1}H NMR ([D$_6$]acetone, 200 MHz): δ = 2.87 (m, 6H, PC*H*CH$_3$), 1.27 [m, 36H, PCHC*H*$_3$], −2.85 [t, *J*(PH) = 30.0 Hz, 1H, OsH]. – ^{31}P NMR ([D$_6$]acetone, 80.9 MHz): δ = 25.76 (s; d in off-resonance). – $C_{20}H_{43}ClOOsP_2S_2$ (651.4): calcd. C 36.88, H 6.66; found C 36.94, H 6.49.

4. *Preparation of [RuHI(CO)(PiPr$_3$)$_2$]* (**6**): A solution of 171 mg (0.35 mmol) of **1** in 10 ml of dichloromethane/acetone (1:1) was treated with 50 mg (0.37 mmol) of LiI and stirred for 2 h at room temp. The solvent was removed and the residue extracted with 20 ml of benzene. The extract was concentrated to ca. 0.5 ml, and then 4 ml of 2-propanol was added. After standing for a few hours, red air-sensitive crystals precipitated which were washed twice with 1 ml of 2-propanol (−30°C) and dried in vacuo; yield 202 mg (87%); m.p. 107°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1910 cm^{-1} [ν(CO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 2.66 (m, 6H, PC*H*CH$_3$), 1.22 [dvt, *N* = 13.2, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.21 [dvt, *N* = 16.0, *J*(HH) = 7.6 Hz, 18H, PCHC*H*$_3$], −23.57 [t, *J*(PH) = 20.0 Hz, 1H, RuH]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 201.98 [t, *J*(PC) = 14.1 Hz, CO], 26.76 (vt, *N* = 21.4 Hz, P*C*HCH$_3$), 20.59, 20.12 (both s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162 MHz): δ = 57.55 (s; d in off-resonance). – $C_{19}H_{43}IOP_2Ru$ (577.6): calcd. C 39.51, H 7.52; found C 39.64, H 7.61; mol. mass 578 (MS).

5. *Preparation of [OsHI(CO)(PiPr$_3$)$_2$]* (**7**): Analogously as described for **6**, by using 200 mg (0.35 mmol) of **2** as starting material; deep red crystals; yield 171 mg (85%). – IR (C_6H_6): $\tilde{\nu}$ = 1890 cm^{-1} [ν(CO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 2.84 (br. m, 6H, PC*H*CH$_3$), 1.26 (br. m, 36H, PCHC*H*$_3$), −29.82 (br., 1H, OsH). – ^{31}P NMR (C_6D_6, 162 MHz): δ = 47.57 (br. s). – $C_{19}H_{43}IOOsP_2$ (666.7): calcd. C 34.23, H 6.51; found C 34.38, H 6.51; mol. mass 668 (MS).

6. *Preparation of [RuI(CO)(PiPr$_3$)$_2$(η^2-S$_2$CH)]* (**8**): Analogously as described for **3**, by using 100 mg (0.17 mmol) of **6** and 0.1 ml (1.7 mmol) of CS_2 as starting materials; deep red crystalline solid; yield 108 mg (84%). – IR (KBr): $\tilde{\nu}$ = 1920 cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 11.18 [t, *J*(PH) = 3.6 Hz, 1H, S_2CH], 2.85 (m, 6H, PC*H*CH$_3$), 1.41 [dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.37 [dvt, *N* = 13.2, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 230.53 [t, *J*(PC) = 7.0 Hz, S_2CH], 207.08 [t, *J*(PC) = 12.9 Hz, CO], 27.51 (vt, *N* = 24.6 Hz, P*C*HCH$_3$), 20.93, 20.89 (both s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 30.81 (s). – $C_{20}H_{43}IOP_2RuS_2$ (653.7): calcd. C 36.75, H 6.64; found C 36.90, H 6.77.

7. *Preparation of [OsI(CO)(PiPr$_3$)$_2$(η^2-S$_2$CH)]* (**9**): Analogously as described for **3**, by using 113 mg (0.17 mmol) of **7** and 0.1 ml (1.7 mmol) of CS_2 as starting materials; deep red crystalline solid; yield 82 mg (72%). – IR (KBr): $\tilde{\nu}$ = 1910 cm^{-1} [ν(CO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 12.19 [t, *J*(PH) = 3.2 Hz, 1H, S_2CH], 2.93 (m, 6H, PC*H*CH$_3$), 1.36 [dvt, *N* = 12.8, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.26 [dvt, *N* = 12.8, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 225.82 [t, *J*(PC) = 4.6 Hz, S_2CH], 184.63 [t, *J*(PC) = 10.1 Hz, CO], 27.70 (vt, *N* = 24.9 Hz, P*C*HCH$_3$), 20.99, 20.90 (both s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162 MHz): δ = −8.65 (s). – $C_{20}H_{43}IOOsP_2S_2$ (742.8): calcd. C 32.34, H 5.85; found C 32.50, H 5.64.

8. *Preparation of [RuCl$_2$(CO)(PiPr$_3$)$_2$]* (**10**): A suspension of 2.0 g (7.6 mmol) of $RuCl_3 \cdot 3\,H_2O$ in 75 ml of methanol was treated at 60°C with 5 ml (29 mmol) of P*i*Pr$_3$ and heated for 24 h under reflux. After cooling to 25°C, the orange-yellow precipitate of **1** was filtered off; yield 2.15 g (70%). The filtrate was concentrated in vacuo to ca. 20 ml, and the solution was then stored for 3 h at 0°C. Dark red crystals formed which were separated, repeatedly washed with small amounts of methanol (−30°C) and dried; yield 487 mg (12%). – IR (KBr): $\tilde{\nu}$ = 1920 cm^{-1} [ν(CO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 2.84 (m, 6H, PC*H*CH$_3$), 1.28 [dvt, *N* = 13.3, *J*(HH) = 6.7 Hz, 36H, PCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 206.62 [t, *J*(PC) = 12.9 Hz, CO], 23.73 (vt, *N* = 20.5 Hz, P*C*HCH$_3$), 19.99 (s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162 MHz): δ = 43.02 (s). – $C_{19}H_{42}Cl_2OP_2Ru$ (520.5): calcd. C 43.84, H 8.07; found C 43.66, H 8.10; mol. mass 520 (MS).

9. *Preparation of [RuCl$_2$(CO)$_2$(PiPr$_3$)$_2$]* (**11**). – (a) A slow stream of CO was passed for 2 min through a solution of 75 mg (0.14 mmol) of **10** in 5 ml of dichloromethane. After the solution had been stirred for 15 min at room temp., it was concentrated to ca. 0.5 ml in vacuo, and then 3 ml of ether was added. A yellow crystalline solid precipitated which was filtered off, washed with ether and dried in vacuo; yield 68 mg (86%). – (b) A solution of 200 mg (0.76 mmol) of $RuCl_3 \cdot 3\,H_2O$ in 20 ml of 2-methoxyethanol was stirred for 30 min at 80°C under CO. After cooling to room temp., the solution was concentrated to ca. 10 ml, and then 0.3 ml (1.52 mmol) of P*i*Pr$_3$ was added. Yellow crystals formed which were repeatedly washed with small amounts of methanol and dried in vacuo; yield 397 mg (96%). – IR (KBr): $\tilde{\nu}$ = 1978 cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.74 (m, 6H, PC*H*CH$_3$), 1.43 [dvt, *N* = 13.4, *J*(HH) = 6.9 Hz, 36H, PCHC*H*$_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 201.72 [t, *J*(PC) = 12.5 Hz, CO], 24.27 (vt, *N* = 22.5 Hz, P*C*HCH$_3$), 19.43 (s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 37.49 (s). – $C_{20}H_{42}Cl_2O_2P_2Ru$ (548.6): calcd. C 43.79, H 7.66; found C 43.88, H 7.59.

10. *Preparation of [$RuCl_2(CO)(PiPr_3)(\eta^2$-$S_2CPiPr_3)$]* (**12**): A solution of 60 mg (0.12 mmol) of **10** in 1 ml of chloroform was treated dropwise with 0.1 ml (1.7 mmol) of CS_2 and stirred for 48 h at room temp. The solution was concentrated in vacuo to ca. 0.3 ml, and then 2 ml of ether was added. Dark (almost black) crystals precipitated which were separated, repeatedly washed with ether and dried in vacuo; yield 68 mg (86%); m.p. 207°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1932 cm^{-1} [ν(CO)], 1064 [ν(CS)]. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.11 (m, 3H, PC*H*CH_3), 2.76 (m, 3H, P'C*H*CH_3), 1.53 [dd, *J*(PH) = 16.0 Hz, *J*(HH) = 8.0 Hz, 18H, PCHC*H*$_3$], 1.35 [dd, *J*(PH) = 12.0 Hz, *J*(HH) = 8.0 Hz, 9H, P'CHC*H*$_3$], 1.32 [dd, *J*(PH) = 16.0 Hz, *J*(HH) = 8.0 Hz, 9H, P'CHC*H*$_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 224.15 [dd, *J*(PC) = 30.2 Hz, *J*(P'C) = 5.7 Hz, S_2C], 195.75 [d, *J*(PC) = 14.1 Hz, CO], 25.77 [d, *J*(PC) = 22.1 Hz, P'*C*HCH$_3$], 21.65 [d, *J*(PC) = 39.2 Hz, P*C*HCH$_3$], 19.64, 19.30 (both s, P'CH*C*H$_3$), 16.91 (s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 54.18 (s, S_2CP), 36.83 (s, P'). – $C_{20}H_{42}Cl_2OP_2RuS_2$ (594.5): calcd. C 40.40, H 7.06; found C 40.52, H 7.12; mol. mass 594 (MS).

11. *Preparation of [$OsH(SPh)(CO)(MeSCN)(PiPr_3)_2$]* (**14**): A solution of 122 mg (0.19 mmol) of **13** in 5 ml of benzene was treated with 20 μl (0.3 mmol) of MeSCN and stirred for 5 min at room temp. The solution was concentrated to ca. 0.5 ml in vacuo, and then 3 ml of methanol was added. White crystals precipitated which were filtered off, washed with small amounts of methanol (−30°C) and dried in vacuo; yield 115 mg (84%). – IR (KBr): $\tilde{\nu}$ = 2150 cm^{-1} [ν(CN)], 1895 [ν(CO)]. – ^1H NMR ($CDCl_3$, 90 MHz): δ = 2.75 (m, 6H, PC*H*CH_3), 1.40 [dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 36H, PCHC*H*$_3$], 1.40 (s, 3H, MeSCN), −15.30 [t, *J*(PH) = 18.0 Hz, 1H, OsH]. – ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ = 24.43 (s; d in off-resonance). – $C_{27}H_{51}NOOsP_2S_2$ (722.0): calcd. C 44.92, H 7.12, N 1.94; found C 44.36, H 7.02, N 1.98.

12. *Preparation of [$OsH(CO)(PiPr_3)_2\{\eta^2$-(S,N)-MeNC-(S)SPh}]* (**15a**, **15b**): A solution of 140 mg (0.22 mmol) of **13** in 5 ml of benzene was treated with 20 mg (0.27 mmol) of MeNCS and stirred for 10 h at room temp. The solution was worked up as described for **14**. Light yellow air-stable crystals were isolated; yield 132 mg (85%). Owing to the relative intensities of the ^1H-NMR signals, the ratio of **15a**:**15b** was 3:2 (60:40). – IR (KBr): $\tilde{\nu}$ = 1890 cm^{-1} [ν(CO)]. – ^1H NMR (C_6D_6, 400 MHz): Isomer **15a**: δ = 7.30 (m, 5H, SC_6H_5), 3.46 (s, 3H, NCH_3), 2.59 (m, 6H, PC*H*CH_3), 1.22 [dvt, *N* = 14.0, *J*(HH) = 6.8 Hz, 36H, PCHC*H*$_3$], −15.44 [t, *J*(PH) = 20.8 Hz, 1H, OsH]; isomer **15b**: δ = 7.30 (m, 5H, SC_6H_5), 2.97 (s, 3H, NCH_3), 2.26 (m, 6H, PC*H*CH_3), 1.30 [dvt, *N* = 13.4, *J*(HH) = 6.8 Hz, 36H, PCHC*H*$_3$], −15.02 [t, *J*(PH) = 18.0 Hz, 1H, OsH]. – ^{13}C NMR (C_6D_6, 100.6 MHz): Isomer **15a**: δ = 184.43 [t, *J*(PC) = 9.1 Hz, CO], 175.79 [t, *J*(PC) = 3.5 Hz, NCS], 136.67, 129.34, 129.13, 127.31 (all s, C_6H_5), 44.84 (s, CH_3N), 26.75 [vt, *N* = 24.6 Hz, P*C*HCH$_3$], 19.75, 19.18 (both s, PCH*C*H$_3$); isomer **15b**: δ = 186.88 [t, *J*(PC) = 10.4 Hz, CO], 182.51 [t, *J*(PC) = 4.7 Hz, NCS], 137.14, 129.65, 129.23, 128.82 (all s, C_6H_5), 43.70 (s, CH_3N), 26.64 (vt, *N* = 22.7 Hz, P*C*HCH$_3$), 20.57, 20.37 (both s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162 MHz); isomer **15a**: δ = 24.69 (s; d in off-resonance); isomer **15b**: δ = 27.67 (s; d in off-resonance). – $C_{27}H_{51}NOOsP_2S_2$ (721.9): calcd. C 44.92, H 7.12, N 1.94; found C 44.68, H 7.15, N 1.77; mol. mass 723 (MS). – If the reaction mixture was stirred for 15 min (instead of 10 h), the isolated solid consisted of isomer **15a**. It was used to obtain single crystals for the crystallograpic study.

13. *Preparation of [$OsH(CO)(PiPr_3)(\eta^2$-$S_2COMe)$]* (**16**): A solution of 110 mg (0.19 mmol) of **2** in 10 ml of benzene was treated dropwise with 195 μl (0.20 mmol) of a 1 N solution of CH_3ONa in methanol. After the solution had been stirred for 2 min at room temp., 0.5 ml of CS_2 was added. The reaction mixture was stirred for 15 min and then concentrated to dryness in vacuo. The residue was exctracted with 10 ml of dichloromethane, the extract was concentrated to ca. 0.5 ml, and 2 ml of hexane was added. After the solution had been stored for 12 h at −78°C, a yellow microcrystalline solid precipitated which was washed with hexane (−30°C) and dried in vacuo; yield 47 mg (58%). – IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1} [ν(OsH)], 1885 [ν(CO)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 3.59 (s, 3H, OCH_3), 2.54 (m, 6H, PC*H*CH_3), 1.29 [dvt, *N* = 13.2, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.22 [dvt, *N* = 12.8, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], −13.85 [t, *J*(PH) = 20.0 Hz, 1H, OsH]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 222.90 [t, *J*(PC) = 4.0 Hz, S_2C], 184.78 [t, *J*(PC) = 9.5 Hz, CO], 54.78 (s, OCH_3), 27.23 (vt, *N* = 25.2 Hz, P*C*HCH$_3$), 20.52, 19.42 (both s, PCH*C*H$_3$). – ^{31}P NMR (C_6D_6, 162 MHz): δ = 24.77 (s; d in off-resonance). – $C_{21}H_{46}O_2OsP_2S_2$ (646.9): calcd. C 39.01, H 7.19; found C 39.37, H 7.24.

14. *Preparation of [$OsH(CO)(PiPr_3)_2(\eta^2$-$O_2CH)$]* (**17**). – (a) A solution of 90 mg (0.16 mmol) of **2** in 5 ml of benzene was treated under CO_2 dropwise with 160 μl (0.16 mmol) of a 1 N solution of CH_3ONa in methanol. After the solution had been stirred for 15 min at room temp., the solvent was removed and the residue

Table 1. Crystallographic data for **4**, **12** and **15a**

	4	**12**	**15a**
Formula	$C_{20}H_{43}ClOOsP_2S_2$	$C_{20}H_{42}OP_2S_2Cl_2Ru$	$C_{27}H_{51}NOOsP_2S_2$
Mol. mass	651.296	596.61	721.97
Cryst size [mm]	0.2 × 0.15 × 0.35	0.4 × 0.6 × 0.25	0.45 × 0.6 × 0.25
Cryst system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	13.097(4)	18.279(1)	8.844(1)
b [Å]	8.464(1)	8.774(1)	11.555(2)
c [Å]	23.772(8)	18.395(1)	16.459(2)
α [°]	90	90	88.12(1)
β [°]	98.04(1)	109.83(1)	78.52(1)
γ [°]	90	90	78.06(1)
V [Å^3]	2665	2775.3(3)	1612.6(3)
Z	4	4	2
$d_{calcd.}$ [g cm^{-3}]	1.624	1.428	1.478
Diffractometer	Enraf-Non. CAD4	STOE Stadi 4	STOE Stadi 4
Radiation (graphite-monochromated)	Mo K_α (0.70930 Å)	Mo K_α (0.70930 Å)	Mo K_α (0.70930 Å)
T [K]	293	293	293
μ [cm^{-1}]	51.7	10.2	44.0
h, *k*, *l*	13, 9, ±25	±22, 11, 23	−11/12, ±16, 23
Scan method	*ω*/*θ*	*θ*/*θ*	*Wyckoff*
2θ(max) [°]	44	55	60
absorption correction	ψ scan	ψ scan	ψ scan
Total no. of reflexions scanned	3703	9982	17157
No. of unique reflexions	3521	6370	9388
No. of observed reflexions [$F_0 > 3\sigma(F_0)$]	2747	5704	9134
No. of parameters refined	248	254	308
R	0.019	0.045	0.022
R_w	0.020	0.037	0.021
Reflexions/parameter ratio	11.1	22.46	29.66
Residual electron density [e Å^{-3}]	+0.644/−0.413	+1.57/−1.40	+0.96/−0.99

extracted with 10 ml of dichloromethane. The extract was concentrated to ca. 0.5 ml in vacuo, and 3 ml of methanol was added. After the solution had been stored for 2 h at −78 °C, white crystals precipitated which were washed with small amounts of methanol (−30 °C) and dried in vacuo; yield 76 mg (82%). – (b) A solution of 115 mg (0.20 mmol) of **2** in 10 ml of dichloromethane/methanol (1:1) was treated with 20 mg (0.40 mmol) of HCO_2Na and stirred for 15 min at room temp. The solution was worked up as described for (a); yield 106 mg (91%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1875 cm^{-1} [ν(CO)], 1555 [ν_{as}(CO)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 8.80 (br. s, 1H, O_2CH), 2.36 (m, 6H, $PCHCH_3$), 1.28 [dvt, N = 13.6, J(HH) = 7.2 Hz, 18H, $PCHCH_3$], 1.21 [dvt, N = 13.6, J(HH) = 6.8 Hz, 18H, $PCHCH_3$], −21.21 [t, J(PH) = 16.0 Hz, 1H, OsH]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 183.40 [t, J(PC) = 7.0 Hz, CO], 173.46 (s, O_2CH), 25.95 (vt, N = 24.7 Hz, $PCHCH_3$), 20.33, 19.62 (both s, $PCHCH_3$). – ^{31}P NMR (C_6D_6, 162 MHz): δ = 39.55 (s; d in off-resonance). – $C_{20}H_{44}O_3OsP_2$ (584.8): calcd. C 41.08, H 7.60; found C 41.22, H 7.67.

15. *X-ray Structure Determination of Compounds* **4**, **12** *and* **15a**[17]: Single crystals were grown by slow diffusion of methanol into benzene solutions of **4** and **15a**, or of ether into a chloroform solution of **12**. Crystal-data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86 and SHELXTL PLUS). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method. The positions of the hydrogen atoms (with the exception of H1 in **4**) were calculated according to ideal geometry (distance C–H = 0.95 Å) and were refined by the riding method with fixed isotropic U values. For other details see Table 1.

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[17] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58482, the names of the authors, and the journal citation.

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