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Five-Coordinate Complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) as Precursors for the Preparation of New Hydrido− and Alkenyl−Metallothiol and Monothio−β-Diketonato Derivatives

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The five-coordinate complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os (**1**), Ru (**2**)) react with NaSH to give the unsaturated hydrido−metallothiol derivatives $MH(SH)(CO)(P^iPr_3)_2$ (M = Os (**3**), Ru (**4**)). Complexes **3** and **4** react with CO to afford the *cis*-dicarbonyl compounds $MH(SH)(CO)_2(P^iPr_3)_2$ (M = Os (**5**), Ru (**6**)). Similarly, the reaction of **3** with $P(OMe)_3$ leads to $OsH(SH)(CO)\{P(OMe)_3\}(P^iPr_3)_2$ (**7**). Treatment of **3** with 1 equiv of acetylenedicarboxylic methyl ester affords $OsH\{SC(CO_2CH_3)CHC(OCH_3)O\}(CO)(P^iPr_3)_2$ (**8**), which is the result of the *trans* addition of the S−H bond of **3** to the carbon−carbon triple bond of the alkyne. The structure of **8** was determined by X-ray investigation. The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying apical positions. The equatorial plane is formed by the bidentate ligand, which acts with a bite angle of 89.49(12)°, the hydrido ligand *trans*-disposed to the oxygen atom, and the carbonyl group *trans*-disposed to the sulfur atom. Acetylenedicarboxylic methyl ester also reacts with **4** by insertion of the carbon−carbon triple bond into the S−H bond. However, in the resulting monothio-β-diketonato derivative $RuH\{SC(CO_2CH_3)CHC(OCH_3)O\}(CO)(P^iPr_3)_2$ (**9**) the hydrido ligand lies *trans* to the sulfur atom. In solution, complex **9** isomerizes into **10**, containing the hydrido ligand *trans*-disposed to the oxygen atom of the chelate group. The stereochemistry of **10** was corroborated by X-ray investigation. The geometry of **10** is the same as that of **8**, and the structural parameters of both molecules are statistically identical. Phenylacetylene and methylpropiolate, in contrast to acetylenedicarboxylic methyl ester, react with **3** and **4** by insertion of the carbon−carbon triple bonds into the M−H bonds to give the unsaturated alkenyl−metallothiol complexes M{(*E*)-CH=CHPh}$(SH)(CO)(P^iPr_3)_2$ (M = Os (**11**), Ru (**12**)) and Ru{(*E*)-CH=$CHCO_2CH_3\}(SH)(CO)(P^iPr_3)_2$ (**13**).

Introduction

Metallothiols, the inorganic counterpart of the organic mercaptans, are a class of compounds characterized by the presence of the M−SH functional group,[1,2] which are presently attracting considerable interest not only because they are structurally related to metal sulfide hydrodesulfurization catalysts[3] but also because they provide model compounds for biological systems[4] involved inter alia in nitrogen fixation and hydrogenation processes.

Previously, we have reported the synthesis of the five-coordinate compounds $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru),[5] which are active and highly selective catalysts for the reduction of unsaturated organic substrates[6] and for the addition of $HSiEt_3$ to phenylacetylene.[7] These compounds have also been the master key for the development of an extensive organometallic chemistry including mono- and binuclear tetrahydridoborate,[8] dihydrogen,[9] polyhydrido,[10] alkynyl,[11] alkenyl,[12] acetatovinyl,[13] carbene,[14] vinylidene,[15] π-butadiene,[16] acyl,[17] aryl,[18] and cyclopentadienyl[19] derivatives.

We now prove that the complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) are also useful starting materials to prepare new metallothiol complexes. This paper describes the synthesis and characterization of new five- and six-coordinate hydrido− and alkenyl−metallothiol compounds and the unprecedented insertion of acetylenedicarboxylic methyl ester into the S-H bond of the complexes $MH(SH)(CO)(P^iPr_3)_2$ (M = Os, Ru).

Results and Discussion

1. Synthesis and Characterization of Five- and Six-Coordinate Hydrido−Metallothiol Complexes.

Treatment at room temperature of tetrahydrofuran solutions of the chloro−hydrido complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os (**1**), Ru (**2**)) with NaSH gives, after solvent removal, sticky residues. Toluene extraction of the residues and filtration to remove NaCl afford solutions from which the five-coordinate hydrido−metallothiol complexes $MH(SH)(CO)(P^iPr_3)_2$ (M = Os (**3**),

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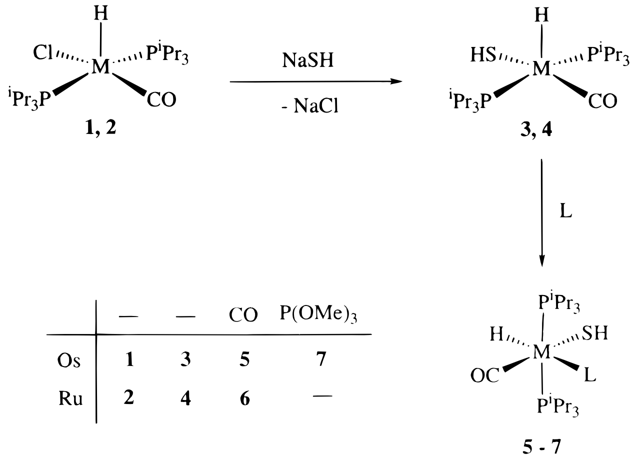
Scheme 1



	—	—	CO	$P(OMe)_3$
Os	1	3	5	7
Ru	2	4	6	—

Ru (**4**)) were isolated (Scheme 1) as orange solids in 83% (**3**) and 66% (**4**) yield. Complexes **3** and **4** are very air-sensitive solids. However, they are stable for up to several months if kept in argon at 0 °C. In solution, they are stable under argon atmosphere only a few days.

In the ^1H NMR spectra of **3** and **4**, the most noticeable resonances are those corresponding to the −SH protons and hydrido ligands, which appear at 4.14 (**3**) and 1.76 (**4**) ppm and at −23.25 (**3**) and −20.71 (**4**) ppm as triplets with H−P coupling constants of 18.7 (**3**) and 17.4 (**4**) Hz and 14.8 (**3**) and 18.0 (**4**) Hz, respectively. Although complexes **3** and **4** are coordinatively unsaturated and the −SH group shows a high tendency to act as bridging

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ligand,[20] the multiplicity of the −SH resonances suggests that they are monomeric in solution. Furthermore, the chemical shifts of the hydrido ligands and the stretching frequencies of the carbonyl groups in the IR spectra in Nujol (1884 (**3**) and 1900 (**4**) cm^{-1}) agree well with those previously reported for the starting complexes **1** (−31.92 ppm and 1886 cm^{-1} in benzene solution) and **2** (−24.20 ppm and 1910 cm^{-1} in benzene solution) for which square-pyramidal arrangements of ligands around of the metallic centers have also been proposed. The T-shape disposition of the hydrido, carbonyl, and π-donor ligand (SH) with the carbonyl group *trans*-disposed to the −SH ligand seems to be the result of an electronic push−pull mechanism between the donor and the acceptor ligands.[21] The $^{31}P\{^1H\}$ NMR spectra show singlets at 44.6 (**3**) and 61.0 (**4**) ppm.

We note that the five-coordinate hydrido−metallothiol complex $RuH(SH)(PPh_3)_3$ has been previously prepared by reaction of $RuH_2(PPh_3)_4$ with H_2S.[1m]

Six-coordinate hydrido−metallothiol complexes can be prepared by reaction of **3** and **4** with non bulky Lewis bases such as CO and $P(OMe)_3$ (Scheme 1). Under carbon monoxide atmosphere, the diethyl ether solutions of **3** and the pentane solutions of **4** afford the *cis*-dicarbonyl derivatives $OsH(SH)(CO)_2(P^iPr_3)_2$ (**5**) and $RuH(SH)(CO)_2(P^iPr_3)_2$ (**6**), respectively. These compounds were isolated as white solids in 89% (**5**) and 41% (**6**) yield. Similar to the reactions of **3** and **4** with carbon monoxide, complex **3** adds trimethyl phosphite to give $OsH(SH)(CO)\{P(OMe)_3\}(P^iPr_3)_2$ (**7**), which was also isolated as a white solid in 78% yield.

The *cis*-relative position of the carbonyl ligands in **5** and **6** was inferred from the IR spectra, which show two strong $\nu(CO)$ bands at 1972 and 1907 cm^{-1} (**5**), and 1955 and 1910 (**6**) cm^{-1}. The −SH resonances appear in the high-field region of the ^1H NMR spectra, at −2.46 (**5**) and −2.96 (**6**) ppm, in agreement with those previously reported for other six-coordinate hydrochalcogenide complexes.[1v] In contrast to **3** and **4**, the −SH hydrogen atom of **5** and **6** shows nuclear spin coupling with the corresponding hydrido ligands. Thus, the −SH resonances are observed as doublets of triplets with H−H and H−P coupling constants of 6.0 (**5**) and 4.5 (**6**) Hz and 1.2 (**5**) and 1.5 (**6**) Hz, respectively. The resonances of the hydrido ligands appear at −6.65 (**5**) and −6.14 (**6**) ppm as double triplets with H−P coupling constants of 21.0 (**5**) and 20.7 (**6**) Hz. The $^{31}P\{^1H\}$ NMR spectra show singlets at 22.2 (**5**) and 57.8 (**6**) ppm.

The spectroscopic data obtained for **7** support the octahedral structure proposed in Scheme 1. The $^{31}P\{^1H\}$ NMR spectrum consists of a triplet at 102.2 ppm and a doublet at 13.5 ppm ($J_{P-P} = 18$ Hz), in agreement with a phosphite ligand *cis* to two equivalent triisopropylphosphine ligands. The proposed *trans* disposition of the hydrido and phosphite ligands is supported by the ^1H NMR spectrum, which contains a doublet ($J_{H-P'} = 137.1$ Hz) of triplets ($J_{H-P} = 25.6$ Hz) of doublets ($J_{H-H} = 5.1$ Hz) at −8.39 ppm. As for **5** and **6**, the high-field region of this spectrum also exhibits the −SH resonance, which is observed at −2.40 ppm as a doublet ($J_{H-P'} = 18.6$ Hz) of doublets ($J_{H-H} = 5.1$ Hz), as a result from the coupling with the hydrido ligand and the phosphorus of the phosphite. Coupling with the phosphorus of the triisopropylphosphine is not observed.

For saturated hydrocarbons, the values of the vicinal ^3J coupling constants are dependent on the dihedral angle between the coupled nuclei, according to the Karplus curves. Thus, the coupling constants are largest for $\Phi = 0°$ or 180°, and smallest for $\Phi = 90°$.[22] The extrapolation of the Karplus relationship into our hydrido−metallothiol compounds permits us to make some interesting conclusions about the disposition of −SH group in **3**−**7**.

As previously mentioned, the −SH proton of **3** and **4** shows nuclear spin coupling with the phosphorus nuclei (about 18 Hz) while coupling with the hydrido ligand is not observed. This suggests that the S-H direction should be perpendicular to the M-H direction with the S-H bond *pseudo*-parallel to P−M−P direction. Furthermore, the equivalence observed in the $^{31}P\{^1H\}$ NMR spectra for the phosphine ligands suggests that a fast change in the orientation of the −SH group ocurrs.

In contrast to **3** and **4**, the −SH proton of **5**−**7** shows nuclear spin coupling with the hydrido ligand (about 5 Hz) while the values of H−P (P = P^iPr_3) coupling constants are zero (**7**) or significantly smaller than those found for **3** and **4** (about 1.5 *versus* 18 Hz). Furthermore, the value of the H−P′ (P′ = $P(OMe)_3$) coupling constant found in **7** (18.6 Hz) is similar to the values of H−P (P = P^iPr_3) coupling constants in **3** and **4**. These data seem to indicate that, in contrast to **3** and **4**, the S-H bond of **5**−**7** is not parallel to the P^iPr_3−M−P^iPr_3 direction but perpendicular.

2. Insertion of $CH_3O_2C-C\equiv C-CO_2CH_3$ into the S−H Bond of 3 and 4. The addition of a stoichiometric amount of acetylenedicarboxylic methyl ester to a tetrahydrofuran solution of **3** leads to the monothio-β-diketonato complex $\overline{\mathrm{OsH\{SC(CO_2CH_3)CHC(OCH_3)O}}\}(CO)(P^iPr_3)_2$ (**8**, in Scheme 2), which is a result of the unprecedented insertion of the carbon−carbon triple bond of the alkyne into the S-H bond of **3**. Complex **8** was isolated as red crystals in 86% yield.

Figure 1 shows a representation of the molecule of **8**. Selected bond distances and angles are listed in Table 1. Although the hydrido ligand could not be located, the presence of this ligand in the complex is supported by the IR and ^1H and $^{31}P\{^1H\}$ NMR spectra. The IR spectrum in Nujol shows a $\nu(Os-H)$ absorption at 2177 cm^{-1}, while the ^1H NMR spectrum in benzene-d_6 contains a triplet with a H−P coupling constant of 16.2 Hz at −20.26 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 22.7 ppm, which is split into a doublet, under off-resonance conditions, as a result from the coupling with the hydrido ligand.

The coordination geometry around the osmium atom could be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying the apical positions (P(1)−Os−P(2) = 171.17(5)°). The equatorial plane is formed by the bidentate ligand, which acts with a bite angle O(2)−Os−S of 89.49(12)°, the hydrido ligand *trans*-disposed to O(2) and the carbonyl group *trans*-disposed to the sulfur atom (C(1)−Os−S = 170.9(2)°).

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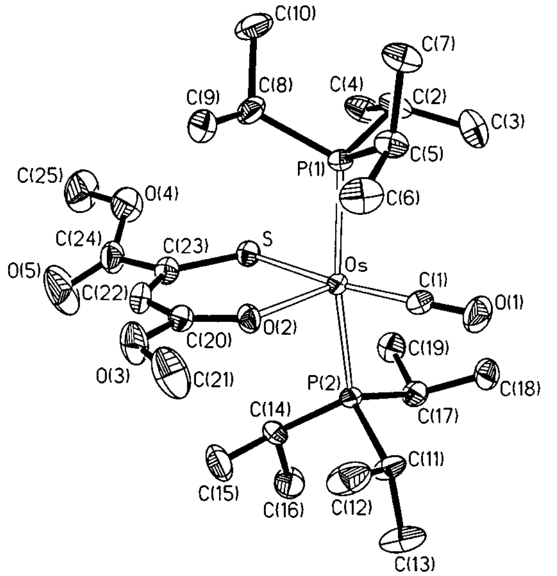
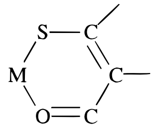
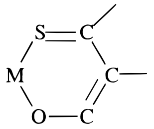


Figure 1. Molecular diagram of complex OsH{SC(CO_2CH_3)CHC(OCH_3)O}(CO)(P^iPr_3)$_2$ (**8**).

The bidentate ligand forms a six-membered, almost planar ring with the osmium atom. The deviations from the best plane are −0.000(1) (Os), 0.003(2) (S), 0.014(5) (O(2)), 0.019(7) (C(20)), −0.039(8) (C(22)), and −0.024(8) (C(23)) Å. The observed interatomic distances in the sequence O(2)−C(20)−C(22)−C(23)−S (1.232(8), 1.428(10), 1.371(10), and 1.703(7) Å) agree well with those found in other monothio-β-diketonato complexes.[23] In this context, is interesting to note that the C$\overset{\cdots}{-}$C bond adjacent to C$\overset{\cdots}{-}$S is slightly shorter than C$\overset{\cdots}{-}$C next to C$\overset{\cdots}{-}$S. It follows that C$\overset{\cdots}{-}$O has more double bond character than C$\overset{\cdots}{-}$S. This indicates that resonance structure **A** makes a greater contribution to the electronic structure than **B**. The preference for tautomer



A



B

A can be rationalized as hydrido preferring the weaker ligand *trans* to itself.

Acetylenedicarboxylic methyl ester also reacts with the ruthenium hydrido−metallothiol complex **4** by insertion of the carbon−carbon triple bond into the S−H bond. However, in the resulting monothio-β-diketonato complex RuH{SC(CO_2CH_3)CHC(OCH_3)O}(CO)(P^iPr_3)$_2$ (**9**), the hydrido ligand lies *trans* to the sulfur atom. In toluene at room temperature, complex **9** is unstable and evolves into the isomer **10** after 15 min. This compound similar to **8**, contains the hydrido ligand *trans*-disposed to the oxygen atom of the chelate group (Scheme 2).

The most significant differences between the spectroscopic data of **9** and **10** are the values of the stretching frequency of the Ru−H bonds in the IR spectra and the chemical shifts of the hydrido ligands in the ^{1}H NMR spectra. The ν(Ru−H) band of **9** appears at 2025 cm^{-1}, while that of **10** is shifted by 55 cm^{-1} to higher wavenumbers (2080 cm^{-1}). The resonance of the hydrido ligand of **9** is observed at −9.16 (t, J_{H-P} = 19.5 Hz) ppm, while the resonance of the hydrido ligand of **10** appears at −17.88 (t, J_{H-P} = 20.1 Hz) ppm, thus shifted by 8.72 ppm to higher field. This difference in chemical shift is similar to that observed (8.78 ppm) between the chemical shifts of the complexes OsH(κ^2-S_2CH)(CO)(P^iPr_3)$_2$ (−12.80 ppm)[9c] and OsH(κ^2-O_2CH)(CO)(P^iPr_3)$_2$ (−21.58 ppm).[24] The $^{31}P\{^1H\}$ NMR spectra of both isomers show singlets at 54.0 (**9**) and 47.5 (**10**) ppm, which are split into doublets under off-resonance conditions.

The definitive characterization of the stereochemistry of **10** was obtained from a X-ray diffraction experiment on a single crystal of the complex. In this case, the hydrido ligand was located in the difference Fourier maps and refined as an isotropic atom together with the rest of the non-hydrogen atoms of the structure, giving a Ru−H(01) distance of 1.55(3) Å. Figure 2 shows a representation of the molecule. Selected bond distances and angles are listed in Table 1. The coordination geometry around the metallic center is the same as that of **8**. Furthermore, the structural parameters of both molecules are statistically identical.

Although transition-metal monothio-β-diketonato complexes are known and the addition of methyl acrylate at the S−H bonds of the complex (η^5-C_5H_5)Ti(μ−SH)$_2$-Mo(CO)$_4$ has been previously reported,[20e] it should be noted that the preparation of this type of compound by insertion of an internal alkyne into the S-H bond of a metallothiol complex has no precedent. Recently, we have also observed that the five-coordinate hydrido−hydroxo complex OsH(OH)(CO)(P^iPr_3)$_2$ reacts with acetylenedicarboxylic methyl ester, similarly to **3** and **4**, to afford the β-diketonato derivative OsH{OC(OCH_3)CHC(CO_2CH_3)O}(CO)(P^iPr_3)$_2$.[25] In contrast to this unsaturated osmium compound, the reaction of the saturated hydroxo complex Ir(η^5-C_5Me_5)(Ph)(OH)(PMe_3) with acetylenedicarboxylic methyl ester leads to Ir(η^5-C_5Me_5)(Ph){(*Z*)-C(CO_2CH_3)=C(CO_2CH_3)OH}(PMe_3), as result of the *cis*-addition of the Ir−O bond to the carbon−carbon triple bond of the alkyne.[26] Similarly, the reactions of the complexes *trans*-Pd(C_6H_4CH=NPh)(NHPh)(PMe_3)$_2$ and *trans*-Pd(C_6H_5)(NHPh) (PMe_3)$_2$ with acetylenedicarboxylic methyl ester result in the *cis*-

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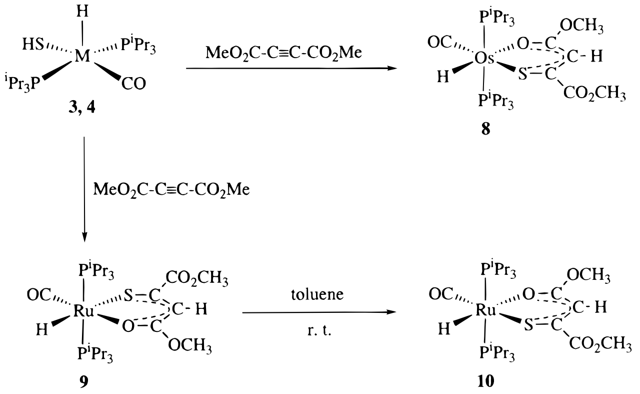
Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complexes $\overline{\mathrm{OsH\{SC(CO_2CH_3)CHC(OCH_3)O}}\mathrm{\}(CO)(PiPr_3)_2}$ (8) and $\overline{\mathrm{RuH\{SC(CO_2CH_3)CHC(OCH_3)O}}\mathrm{\}(CO)(P^iPr_3)_2}$ (10)[a]

	Os	Ru		Os	Ru
M–P(1)	2.385(2)	2.3894(6)	O(2)–C(20)	1.232(8)	1.232(3)
M–P(2)	2.383(2)	2.3871(6)	C(20)–C(22)	1.428(10)	1.442(3)
M–H(01)		1.55(3)	C(20)–O(3)	1.346(8)	1.348(3)
M–C(1)	1.833(7)	1.823(2)	C(22)–C(23)	1.371(10)	1.356(3)
M–O(2)	2.225(4)	2.2275(14)	C(23)–C(24)	1.511(10)	1.513(3)
M–S	2.429(2)	2.4319(6)	C(23)–S	1.703(7)	1.714(2)
C(1)–O(1)	1.171(8)	1.165(3)			
P(1)–M–P(2)	171.17(5)	169.83(2)	C(1)–M–O(2)	99.6(2)	100.77(8)
P(1)–M–H(01)		84.0(8)	C(1)–M–S	170.9(2)	169.98(7)
P(1)–M–C(1)	88.5(2)	88.62(7)	O(2)–M–S	89.49(12)	89.23(4)
P(1)–M–O(2)	93.72(13)	94.31(4)	M–S–C(23)	110.0(2)	110.12(8)
P(1)–M–S	90.02(6)	90.06(2)	S–C(23)–C(24)	114.8(5)	114.9(2)
P(2)–M–H(01)		86.4(8)	C(22)–C(23)–C(24)	113.7(6)	113.6(2)
P(2)–M–C(1)	87.8(2)	87.25(7)	C(20)–C(22)–C(23)	127.7(6)	127.8(2)
P(2)–M–O(2)	94.80(13)	95.59(4)	C(22)–C(20)–O(3)	111.5(6)	111.2(2)
P(2)–M–S	92.35(6)	92.39(2)	O(2)–C(20)–O(3)	118.8(6)	119.6(2)
H(01)–M–C(1)		83.7(8)	C(22)–C(20)–O(2)	129.7(6)	129.3(2)
H(01)–M–O(2)		175.1(8)	M–O(2)–C(20)	131.5(4)	132.03(15)
H(01)–M–S		86.2(8)			

[a] The first set of values (Os) corresponds to the bond distances and angles of the complex **8**; the second set of values (Ru) corresponds to the related parameters observed in complex **10**.

Scheme 2



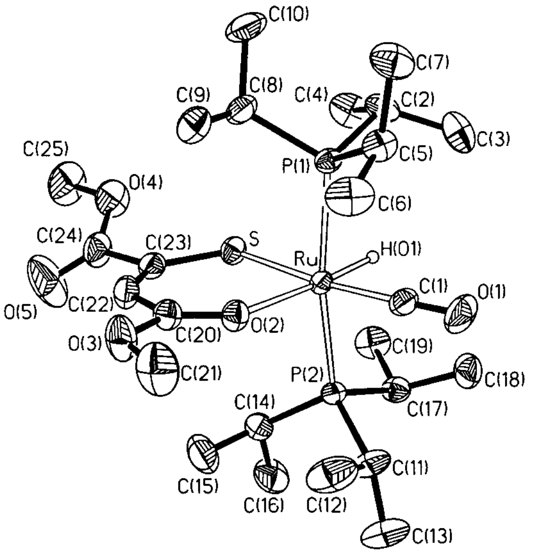
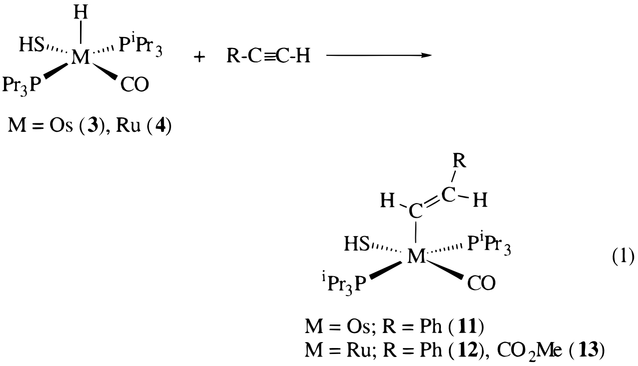


Figure 2. Molecular diagram of complex $\overline{\mathrm{RuH\{SC(CO_2CH_3)CHC(OCH_3)O}}\mathrm{\}(CO)(P^iPr_3)_2}$ (**10**).

insertion of the acetylene into the Pd–N bond.[27] In addition, we must point out the different behavior of **3** and its precursor **1**, which reacts with acetylenedicarboxylic methyl ester by insertion of the alkyne in the Os–H bond to give the alkenyl derivative $\overline{\mathrm{Os\{C[C(O)}}\mathrm{OCH_3]{=}CHCO_2CH_3\}Cl(CO)(P^iPr_3)_2}$.[6c]

3. Synthesis and Characterization of Five-Coordinate Alkenyl–Metallothiol Complexes. Phenylacetylene and methylpropiolate, in contrast to acetylenedicarboxylic methyl ester, react with **3** and **4** by insertion of the carbon–carbon triple bonds into the M–H bonds of these compounds (eq 1). The five-



(1)

coordinate complexes Os{(*E*)-CH=CHPh}(SH)(CO)(P^{i}Pr$_3$)$_2$ (**11**), Ru{(*E*)-CH=CHPh}(SH)(CO)(P^{i}Pr$_3$)$_2$ (**12**), and Ru{(*E*)-CH=CHCO$_2$CH$_3$}(SH)(CO)(P^{i}Pr$_3$)$_2$ (**13**), inorganic counterpart of the organic α, β-unsaturated mercaptans, formed are the first alkenyl–metallothiols isolated.

Complexes **11**–**13** were prepared in 40–60% yield and characterized by elemental analysis and IR and ^{1}H, ^{13}C-{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies. The presence of an alkenyl group with *E* stereochemistry in these compounds is strongly supported by the resonances of the vinylic protons of the unsaturated η^1-carbon ligands in the ^{1}H NMR spectra. The value of the coupling constants between these protons (about 14 Hz for the three derivatives) is characteristic for this arrangement.[12a] Furthermore, the ^{1}H NMR spectra show a triplet between 1.49 and 3.42 ppm, with H–P coupling constant values between 16.2 and 17.7 Hz, which was assigned to the –SH proton. The multiplicity of these resonances indicates that although the complexes are unsaturated, they are also monomeric in solution, as precursors **3** and **4**. In addition, it should be noted that the values of the H−P coupling constants are similar to those found in **3** and **4**, suggesting that in **11**−**13** the disposition of the S-H bond could also be *pseudo*-parallel to the P−M−P direction. As in **3** and **4**, the $^{31}P\{^1H\}$ NMR spectra show singlets at 21.2 (**11**), 41.4 (**12**), and 43.2 (**13**) ppm, indicating that the phosphine ligands also become equivalent in solution.

In the $^{13}C\{^1H\}$ NMR spectra, the resonances of the α-carbon atom of the alkenyl groups appear at 135.3 (**11**), 152.4 (**12**), and 186.4 (**13**) ppm, as triplets with C−P coupling constants of 3.1 (**11**), 10.8 (**12**), and 10.2 (**13**) Hz. The resonances of the *β*-carbon atoms are observed at 141.5 (**11**), 139.9 (**12**), and 126.2 (**13**) ppm, also as triplets but with C−P coupling constants between 1 and 3 Hz.

Concluding Remarks

This study has revealed that the five-coordinate complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) are useful starting materials for the preparation of new five- and six-coordinate hydrido−metallothiol, six-coordinate monothio-*β*-diketonato, and five-coordinate alkenyl−metallothiol derivatives. Thus, they react with NaSH to afford $MH(SH)(CO)(P^iPr_3)_2$ (M = Os, Ru), which are novel precursors for the preparation of the above-mentioned compounds.

From a methodological point of view, the synthesis of the monothio-*β*-diketonato complexes $MH\{SC(CO_2CH_3)CHC(OCH_3O\}(CO)(P^iPr_3)_2$ (M = Os, Ru) as a result of the unprecedented insertion of the carbon−carbon triple bond of acetylenedicarboxylic methyl ester into the S-H bond of $MH(SH)(CO)(P^iPr_3)_2$ should be pointed out. Phenylacetylene and methylpropiolate, in contrast to the internal alkyne, react by insertion of the carbon−carbon triple bond into the M-H bond to give M{(*E*)-CH=CHR}(SH)(CO)$(P^iPr_3)_2$ (M = Os, Ru), which are the first inorganic counterparts of the organic α,*β*-unsaturated mercaptans.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried using appropriate drying agents and freshly distilled under argon before use. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Unity 300 or on a Bruker 300 AXR spectrometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants (J and N [$N = J(PH) + J(P'H)$ or $J(PC) + J(P'C)$]) are given in hertz. IR data were recorded on a Nicolet 550 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 240C microanalyzer. The starting complexes $OsHCl(CO)(PiPr_3)_2$ and $RuHCl(CO)(PiPr_3)_2$ were prepared by published methods.[5]

Preparation of $OsH(SH)(CO)(P^iPr_3)_2$ (3). A solution of $OsHCl(CO)(P^iPr_3)_2$ (**1**) (470 mg, 0.82 mmol) in THF/CH_3OH (4:1, 15 mL) was treated with NaSH (150 mg, 2.7 mmol). The color of the solution changed immediately from red to dark orange. The mixture was stirred for 5 min at room temperature. The solution was concentrated to dryness; then 15 mL of toluene was added, and the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.5 mL; addition of pentane caused the precipitation of an orange solid. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 393 mg (83%). Anal. Calcd for $C_{19}H_{44}OOsP_2S$: C, 39.84; H, 7.74; S, 5.60. Found: C, 39.58; H, 7.50; S, 6.07.

IR (Nujol, cm^{-1}): ν(Os−H) 1905; ν(CO) 1884. ^1H NMR (300 MHz, C_6D_6): δ 4.14 (t, 1H, $J_{H-P} = 18.7$ Hz, Os−S*H*), 2.45 (m, 6H, PC*H*CH_3), 1.22 (dvt, 36H, $J_{H-H} = 6.9$ Hz, $N = 13.4$ Hz, PCHC*H*$_3$), −23.25 (t, 1H, $J_{H-P} = 14.8$ Hz, Os−*H*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 44.6 (s).

Preparation of $RuH(SH)(CO)(P^iPr_3)_2$ (4). A solution of $RuHCl(CO)(P^iPr_3)_2$ (**2**) (1.10 g, 2.26 mmol) in THF/CH_3OH (2:1, 20 mL) was treated with NaSH (215 mg, 3.8 mmol). The mixture was stirred for 7.5 h at room temperature. The solution was concentrated to dryness; then 10 mL of toluene was added, and the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.5 mL; addition of methanol caused the precipitation of an orange solid. The solvent was decanted, and the solid was washed with methanol and dried in vacuo. Yield: 725 mg (66%). Anal. Calcd for $C_{19}H_{44}OP_2RuS$: C, 47.18; H, 9.17; S, 6.63. Found: C, 46.62; H, 9.49; S, 6.57.

IR (Nujol, cm^{-1}): ν(Ru−H) 2017; ν(CO) 1900. ^1H NMR (300 MHz, C_6D_6): δ 2.35 (m, 6H, PC*H*CH_3), 1.76 (t, 1H, $J_{H-P} = 17.4$ Hz, Ru−S*H*), 1.23 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 13.8$ Hz, PCHC*H*$_3$), 1.21 (dvt, 18H, $J_{H-H} = 7.2$ Hz, $N = 12.9$ Hz, PCHC*H*$_3$), −20.71 (t, 1H, $J_{H-P} = 18.0$ Hz, Ru−*H*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 61.0 (s).

Preparation of $OsH(SH)(CO)_2(P^iPr_3)_2$ (5). CO was bubbled through a stirred solution of $OsH(SH)(CO)(P^iPr_3)_2$ (**3**) (115 mg, 0.20 mmol) in 6 mL of diethyl ether for 10 min. The solution was concentrated to dryness. After the addition of pentane a white solid was formed. The solvent was decanted, and the solid was washed with pentane, and dried in vacuo. Yield: 106 mg (89%). Anal. Calcd for $C_{20}H_{44}O_2OsP_2S$: C, 39.99; H, 7.38; S, 5.34. Found: C, 39.92; H, 7.00; S, 5.63.

IR (Nujol, cm^{-1}): ν(Os−H) 2052; ν(CO) 1972, 1907.^1H NMR (300 MHz, C_6D_6): δ 2.66 (m, 6H, PC*H*CH_3) 1.19 (dvt, 18H, $J_{H-H} = 7.5$ Hz, $N = 14.4$ Hz, PCHC*H*$_3$), 1.17 (dvt, 18H, $J_{H-H} = 7.2$ Hz, $N = 14.1$ Hz, PCHC*H*$_3$), −2.46 (dt, 1H, $J_{H-H} = 6.0$ Hz, $J_{H-P} = 1.2$ Hz, Os−S*H*) −6.65 (td, 1H, $J_{H-P} = 21.0$ Hz, $J_{H-H} = 6.0$ Hz, Os−*H*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 22.2 (s).

Preparation of $RuH(SH)(CO)_2(P^iPr_3)_2$ (6). CO was bubbled through a stirred solution of $RuH(SH)(CO)(P^iPr_3)_2$ (**4**) (119 mg, 0.25 mmol) in 6 mL of pentane for 1 h. The mixture was filtered through Kieselguhr, and then the resulting solution was stored at −78 °C for 24 h. A white solid was formed. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 51.5 mg (41%). Anal. Calcd for $C_{20}H_{44}O_2P_2RuS$: C, 46.95; H, 8.66; S, 6.26. Found: C, 46.95; H, 8.61; S, 6.38.

IR (Nujol, cm^{-1}): ν(Ru−H) 2018; ν(CO) 1955, 1910. ^1H NMR (300 MHz, C_6D_6): δ 2.62 (m, 6H, PC*H*CH_3), 1.20 (dvt, 36H, $J_{H-H} = 7.2$ Hz, $N = 14.1$ Hz, PCHC*H*$_3$), −2.96 (dt, 1H, $J_{H-H} = 4.5$ Hz, $J_{H-P} = 1.5$ Hz, Ru−S*H*), −6.14 (td, 1H, $J_{H-P} = 20.7$ Hz, $J_{H-H} = 4.5$ Hz, Ru−*H*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 57.8 (s).

Preparation of $OsH(SH)(CO)\{P(OMe)_3\}(P^iPr_3)_2$ (7). A solution of $OsH(SH)(CO)(P^iPr_3)_2$ (**3**) (95 mg, 0.16 mmol) in 5 mL of THF was treated with $P(OMe)_3$ (20 μL, 0.17 mmol). The mixture was stirred for 15 min. The solution was concentrated to dryness. After the addition of pentane, a white solid was formed. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 90 mg (78%). Anal. Calcd for $C_{22}H_{53}O_4OsP_3S$: C, 37.92; H, 7.67; S, 4.60 Found: C, 37.56; H, 7.74; S, 4.85.

IR (Nujol, cm^{-1}): ν(Os−H) 2065; ν(CO) 1918. ^1H NMR (300 MHz, C_6D_6): δ 3.35 (d, 9H, $J_{H-P} = 10.5$ Hz, POC*H*$_3$), 2.88 (m, 6H, PC*H*CH_3), 1.33 (dvt, 18H, $J_{H-H} = 7.2$ Hz, $N = 13.2$ Hz, PCHC*H*$_3$), 1.31 (dvt, 18H, $J_{H-H} = 6.0$ Hz, $N = 12.8$ Hz, PCHC*H*$_3$), −2.40 (dd, 1H, $J_{H-P'} = 18.6$ Hz, $J_{H-H} = 5.1$ Hz, Os−S*H*), −8.39 (dtd, 1H, $J_{H-P'} = 137.1$ Hz, $J_{H-P} = 25.6$ Hz, $J_{H-H} = 5.1$ Hz, Os−*H*). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 102.2 (t, $J_{P-P} = 18.0$ Hz), 13.5 (d, $J_{P-P} = 18.0$ Hz).

Preparation of $\overline{OsH[SC(CO_2CH_3)CHC(OCH_3)O}](CO)(PiPr_3)_2$ (8). A solution of $OsH(SH)(CO)(P^iPr_3)_2$ (**3**) (135.0 mg, 0.24 mmol) in 8 mL of THF was treated with acetylenedicarboxylic methyl ester (30 μL, 0.24 mmol). The mixture was stirred for 2 h. The solution was concentrated to dryness. After the addition of pentane, a red solid was formed. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 145 mg (86%). Anal. Calcd for $C_{25}H_{50}O_5OsP_2S$: C, 42.00; H, 7.05; S, 4.49. Found: C, 41.57; H, 7.04; S, 4.96.

IR (Nujol, cm^{-1}): ν(Os−H) 2177; ν(CO) 1895; ν(C=O) 1716. ^{1}H NMR (300 MHz, C_6D_6): δ 7.11 (s, 1H, −C*H*−), 3.30 and 3.35 (both s, each 3H, $CO_2C\mathit{H}_3$), 2.62 (m, 6H, $PC\mathit{H}CH_3$), 1.23 (dvt, 18H, J_{H-H} = 6.6 Hz, *N* = 12.9 Hz, $PCHC\mathit{H}_3$), 1.12 (dvt, 18H, J_{H-H} = 6.3 Hz, *N* = 12.6 Hz, $PCHC\mathit{H}_3$), −20.26 (t, 1H, J_{H-P} = 16.2 Hz, Os−*H*). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 185.7 (t, J_{C-P} = 10.1 Hz, Os*C*O), 168.0 and 167.3 (both s, $\mathit{C}O_2CH_3$), 166.1 (s, $S\mathit{C}(CO_2CH_3)$), 111.6 (s, −*C*H−), 52.2 and 51.7 (both s, $CO_2\mathit{C}H_3$), 25.7 (vt, *N* = 24.4 Hz, $P\mathit{C}HCH_3$), 19.5 and 19.2 (both s, $PCH\mathit{C}H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 22.7 (s, d under off-resonance conditions).

Preparation of $\overline{RuH\{SC(CO_2CH_3)CHC(OCH_3)O}\}(CO)(P^iPr_3)_2$ (9). A solution of $RuH(SH)(CO)(P^iPr_3)_2$ (**4**) (176.4 mg, 0.36 mmol) in 6 mL of pentane was treated with acetylenedicarboxylic methyl ester (53.7 μL, 0.44 mmol). After the mixture was stirred for 5 h, a deep red solid was formed. The solvent was decanted, and the solid was washed twice with pentane and dried in vacuo. Yield: 73.5 mg (32%). Anal. Calcd for $C_{25}H_{50}O_5P_2RuS$: C, 47.99; H, 8.05; S, 5.12. Found: C, 47.66; H, 7.52; S, .5.51.

IR (Nujol, cm^{-1}): ν(Ru−H) 2025; ν(CO) 1908; ν(C=O) 1716. ^{1}H NMR (300 MHz, C_6D_6): δ 6.99 (s, 1H, −C*H*−), 3.39 and 3.19 (both s, each 3H, $CO_2C\mathit{H}_3$), 2.20 (m, 6H, $PC\mathit{H}CH_3$), 1.28 (dvt, 18H, J_{H-H} = 6.9 Hz, *N* = 12.9 Hz, $PCHC\mathit{H}_3$), 1.24 (dvt, 18H, J_{H-H} = 7.2 Hz, *N* = 13.2 Hz, $PCHC\mathit{H}_3$), −9.16 (t, 1H, J_{H-P} = 19.5 Hz, Ru−*H*). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 207.9 (t, J_{C-P} = 14.3 Hz, Ru*C*O), 174.9 and 170.0 (both s, $\mathit{C}O_2CH_3$), 167.0 (s, $S\mathit{C}(CO_2CH_3)$), 107.3 (s, −*C*H−), 52.1 and 51.1 (both s, $CO_2\mathit{C}H_3$), 25.1 (vt, *N* = 18.4 Hz, $P\mathit{C}HCH_3$), 19.5 and 19.1 (both s, $PCH\mathit{C}H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 54.0 (s, d under off-resonance conditions).

Preparation of $\overline{RuH\{SC(CO_2CH_3)CHC(OCH_3)O}\}(CO)(P^iPr_3)_2$ (10). A solution of **9** (102.5 mg, 0.16 mmol) in 5 mL of toluene was stirred for 15 min. The solution was concentrated to dryness. After the addition of methanol, an orange solid was formed. The solvent was decanted, and the orange solid was washed with methanol and dried in vacuo. Yield: 46 mg (45%). Anal. Calcd for $C_{25}H_{50}O_5P_2RuS$: C, 47.99; H, 8.05; S, 5.12. Found: C, 47.80; H, 8.15; S, 5.61.

IR (Nujol, cm^{-1}): ν(Ru−H) 2080; ν(CO) 1909; ν(C=O) 1717. ^{1}H NMR (300 MHz, C_6D_6): δ 7.01 (s, 1H, −C*H*−), 3.36 and 3.32 (both s, each 3H, $CO_2C\mathit{H}_3$), 2.57 (m, 6H, $PC\mathit{H}CH_3$), 1.25 (dvt, 18H, J_{H-H} = 6.7 Hz, *N* = 13.3 Hz, $PCHC\mathit{H}_3$); 1.13 (dvt, 18H, J_{H-H} = 6.6 Hz, *N* = 12.9 Hz, $PCHC\mathit{H}_3$); −17.88 (t, 1H, J_{H-P} = 20.1 Hz, Ru−*H*). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 203.4 (t, J_{C-P} = 13.8 Hz, Ru-*C*O), 169.8 and 169.1 (both s, $\mathit{C}O_2CH_3$), 167.4 (s, $S\mathit{C}(CO_2CH_3)$), 110.4 (s, −*C*H−), 52.0 and 51.1 (both s, $CO_2\mathit{C}H_3$), 25.5 (vt, *N* = 19.6 Hz, $P\mathit{C}HCH_3$), 19.5 and 19.2 (both s, $PCH\mathit{C}H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 47.5 (s, d under off-resonance conditions).

Preparation of Os{(*E*)-CH=CHPh}(SH)(CO)(P^iPr_3)$_2$ (11). A solution of $OsH(CO)(SH)(P^iPr_3)_2$ (**3**) (120 mg, 0.21 mmol) in 6 mL of diethyl ether was treated with PhC≡CH (23 μL, 0.21 mmol). The mixture was stirred for 20 min. The solution was concentrated to dryness, and after the addition of pentane, a dark orange solid was formed. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 78 mg (55%). Anal. Calcd for $C_{27}H_{50}OOsP_2S$: C, 48.05; H, 7.47; S, 4.75. Found: C, 47.61; H, 7.83; S, 5.01.

IR (Nujol, cm^{-1}): ν(CO) 1881; ν(C=C) 1550. ^{1}H NMR (300 MHz, C_6D_6): δ 8.68 (d, 1H, J_{H-H} = 13.8 Hz, Os−C*H*=), 7.30−6.90 (m, 5H, $C_6\mathit{H}_5$), 6.29 (d, 1H, J_{H-H} = 13.8 Hz, =C*H*Ph), 3.42 (t, 1H, J_{H-P} = 17.7 Hz, Os−S*H*), 2.61 (m, 6H, $PC\mathit{H}CH_3$), 1.21 (dvt, 18H, J_{H-H} = 6.6 Hz, *N* = 13.5 Hz, $PCHC\mathit{H}_3$); 1.14 (dvt, 18H, J_{H-H} = 6.3 Hz, *N* = 12.9 Hz, $PCHC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 188.3 (t, J_{C-P} = 9.2 Hz, Os−*C*O), 141.5 (t, J_{C-P} = 1.7 Hz, Os−CH=*C*); 135.3 (t, J_{C-P} = 3.1 Hz, Os-*C*H=C), 128.7, 124.3. 124.0 (all s, C_6H_5), 25.4 (vt, *N* = 24.9 Hz, $P\mathit{C}HCH_3$); 20.2 and 19.5 (both s, $PCH\mathit{C}H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 21.2 (s).

Table 2. Crystal Data and Data Collection and Refinement for $\overline{OsH\{SC(CO_2CH_3)CHC(OCH_3)O}\}(CO)(P^iPr_3)_2$ (8) and $\overline{RuH\{SC(CO_2CH_3)CHC(OCH_3)O}\}(CO)(P^iPr_3)_2$ (10)

	8	**10**
formula	$C_{25}H_{50}O_5OsP_2S$	$C_{25}H_{50}O_5P_2RuS$
mol wt	714.85	625.72
color, habit	red, laminar crystal	orange, irregular block
crystal size, mm	0.52 × 0.12 × 0.06	0.44 × 0.28 × 0.26
space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	8.5239(9)	8.5583(8)
b, Å	11.9327(14)	11.9282(11)
c, Å	15.171(2)	15.2736(13)
α, deg	94.565(10)	94.569(8)
β, deg	97.941(8)	97.478(9)
γ, deg	93.184(6)	92.724(9)
V, Å^3	1520.0(4)	1538.4(3)
Z	2	2
D(calcd), g cm^{-3}	1.562	1.351
μ, mm^{-1}	4.399	0.712
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	$2.7 \le 2\theta \le 50$	$4.2 \le 2\theta \le 50$
temp, K	200	173
no. of data collected	7337	6564
no. of unique data	5327 (R_{int} = 0.0471)	5381 (R_{int} = 0.0152)
no. of params refined	322	326
$R_1{}^a$ ($F_o \ge 4.0\sigma(F_o)$)	0.0382	0.0225
$wR_2{}^b$ (all data)	0.1093	0.0585
S^c	0.983	0.963

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$ (**8**, *a* = 0.0827, *b* = 1.01; **10**, *a* = 0.0394, *b* = 0.01). [c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

Preparation of Ru{(*E*)-CH=CHPh}(SH)(CO)(P^iPr_3)$_2$ (12). A solution of $RuH(CO)(SH)(P^iPr_3)_2$ (**4**) (102 mg, 0.21 mmol) in 6 mL of pentane was treated with PhC≡CH (25.8 μL, 0.25 mmol). After the mixture was stirred for 1.5 min, a dark orange solid was formed. The solvent was decanted, and the solid was washed with pentane and dried in vacuo. Yield: 78 mg (63%). Anal. Calcd for $C_{27}H_{50}OP_2RuS$: C, 55.36; H, 8.60; S, 5.47. Found: C, 54.81; H, 8.82; S, 5.76.

IR (Nujol, cm^{-1}): ν(CO) 1894; ν(C=C) 1595. ^{1}H NMR (300 MHz, C_6D_6): δ 8.94 (d, 1H, J_{H-H} = 13.8 Hz, Ru−C*H*=), 7.28−6.9 (m, 5 H, $C_6\mathit{H}_5$), 6.46 (d, 1H, J_{H-H} = 13.8 Hz, =C*H*Ph), 2.50 (m, 6H, $PC\mathit{H}CH_3$), 1.49 (t, 1H, J_{H-P} = 16.2 Hz, Ru−S*H*), 1.19 and 1.14 (both dvt, 18H, J_{H-H} = 7.2 Hz, *N* = 13.2 Hz, $PCHC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 205.4 (t, J_{C-P} = 13.1 Hz, Ru−*C*O), 152.4 (t, J_{C-P} = 10.8 Hz, Ru−*C*H=C), 139.9 (t, J_{C-P} = 2.1 Hz, Ru-CH=*C*), 135.6 (t, J_{C-P} = 3.5 Hz, C_{ipso}−Ph), 128.9 (s, C_{ortho}−Ph); 124.31 (s, C_{meta}−Ph), 124.26 (s, C_{para}−Ph), 25.2 (vt, *N* = 19.8 Hz, $P\mathit{C}HCH_3$), 20.2 and 19.5 (both s, $PCH\mathit{C}H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 41.4 (s).

Preparation of Ru{(*E*)-CH=CHCO$_2$CH$_3$}(SH)(CO)(P^iPr_3)$_2$ (13). A solution of $RuH(CO)(SH)(P^iPr_3)_2$ (**4**) (78.3 mg, 016 mmol) in 6 mL of pentane was treated with HC≡CCO$_2$CH$_3$ (15.2 μL, 0.18 mmol). After the mixture was stirred for 1 h, a yellow solid was formed. The solvent was decanted, and the yellow solid was washed with pentane and dried in vacuo. Yield: 40 mg (44%). Anal. Calcd for $C_{27}H_{50}O_3P_2RuS$: C, 48.80; H, 8.52; S, 5.60. Found: C, 49.20; H, 8.78; S, 5.61.

IR (Nujol, cm^{-1}): ν(CO) 1909; ν(C=O) 1693; ν(C=C) 1520. ^{1}H NMR (300 MHz, C_6D_6): δ 10.65 (dt, 1H, J_{H-H} = 13.5 Hz,

J_{H-P} = 1.0 Hz, Ru−C*H*═C), 6.34 (dt, 1H, J_{H-H} = 13.5 Hz, J_{H-P} = 1.8 Hz, −CH═C*H*), 3.55 (s, 3H, −CO$_2$C*H*$_3$), 2.42 (m, 6H, PC*H*CH$_3$), 1.58 (t, 1H, J_{H-P} = 16.5 Hz, Ru−S*H*), 1.14 (dvt, 18H, J_{H-H} = 7.2 Hz, *N* = 13.8 Hz, PCHC*H*$_3$), 1.09 (dvt, 18H, J_{H-H} = 6.9 Hz, *N* = 14.0 Hz, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.43 MHz, C$_6$D$_6$): δ 204.3 (t, J_{C-P} = 12.4 Hz, Ru-*C*O), 186.4 (t, J_{C-P} = 10.2 Hz, Ru−*C*H═CH), 162.4 (t, J_{C-P} = 1.6 Hz, −*C*O$_2$CH$_3$), 126.2 (t, J_{C-P} = 2.8 Hz, Ru-CH═*C*), 50.1 (s, −CO$_2$*C*H$_3$), 25.3 (vt, *N* = 20.2 Hz, P*C*HCH$_3$), 20.1 and 19.4 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$): δ 43.2 (s).

Crystal Data for 8 and 10. Crystals suitable for the X-ray diffraction study were grown in a solution of complex **8** in pentane (or **10** in acetone) after storing at −20 °C for 3 days (or at 0 °C for 1 week (**10**)). A summary of the crystal data and refinement parameters is reported in Table 2. The red (**8**) or orange (**10**) crystals (0.52 × 0.12 × 0.06 mm (**8**) and 0.44 × 0.28 × 0.26 mm (**10**)) were glued on a glass fiber and mounted on a Siemens P4 four-circle diffractometer, with graphite-monochromated Mo Kα radiation. A group of 56 reflections in the range 24° ≤ 2θ ≤ 39° (**8**) or 52 reflections in the range 30° ≤ 2θ ≤ 45° (**10**) were carefully centered at 200 (**8**) or 173 K (**10**) and used to obtain the unit cell dimensions by least-squares methods. Three standard reflections were monitored at periodic intervals thoughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.[28] The structures were solved by Patterson (Os atom, SHELXTL-PLUS[29]) (**8**) or direct methods (**10**) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL93[30]). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed (hydrido in **10**) or calculated and refined riding on carbon atoms with common isotropic thermal parameters. Atomic scattering factors, corrected for anomalous dispersion for Os, Ru, and P, were implemented by the program. The refinement converge to R_1 [$F^2 > 2\sigma(F^2)$] = 0.0382 (**8**) or 0.0225 (**10**) and wR_2 (all data) = 0.1093 (**8**) or 0.0585 (**10**).

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles for **8** and **10** (16 pages). Ordering information is given on any current masthead page.

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