

Oxo and thiophosphoramides of niobocene or tantalocene as organometallic ligands: synthesis of heterobimetallic complexes $[\text{Cp}_2\text{M}(\text{CO})(\mu, \eta^1 : \eta^1\text{-PR}_2\text{X})\text{M}'\text{L}_n]$ ($\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{O}$ or S ; $\text{M}' = \text{Cr}, \text{Mo}, \text{W}, \text{Mn}, \text{Fe}$ or Sn)

Sylvine Challet^a, Marek M. Kubicki^a, Jean-Claude Leblanc^a, Claude Moïse^{a,*}, Bernd Nuber^b

^a *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Unité de Recherche associée au CNRS 1685, 6 boulevard Gabriel, F-21000 Dijon, France*

^b *Anorganisch-Chemisches Institut der Universität, W-69120 Heidelberg, Germany*

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Abstract

The phosphido complexes $\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2)$ (with $\text{M} = \text{Nb}$ or Ta and $\text{R} = \text{Me}$ or Ph) react with H_2O_2 or S_8 , leading to the corresponding oxides and sulfides. The oxygen and the sulfur derivatives have similar reactivities towards organic electrophilic reagents such as MeI and MeCOCl . Unlike organometallic electrophilic species, the sulfur derivatives afford a new class of bimetallic complex $[\text{Cp}_2\text{M}(\text{CO})(\mu, \eta^1 : \eta^1\text{-PR}_2\text{S})\text{M}'\text{L}_n]$ ($\text{M}'\text{L}_n = \text{Cr}(\text{CO})_5, \text{Mo}(\text{CO})_5, \text{W}(\text{CO})_5, \text{CpMn}(\text{CO})_2$ or $\text{Fe}(\text{CO})_4$). In contrast, the oxygen compounds react only with organometallic tin complexes such as Bu_3SnCl . The crystallographic analyses of $[\text{Cp}_2\text{Nb}(\text{CO})(\text{PPh}_2\text{SMe})\text{I}]$ and $[\text{Cp}_2\text{Ta}(\text{CO})(\mu, \eta^1 : \eta^1\text{-PMe}_2\text{S})\text{W}(\text{CO})_5]$ are reported and discussed.

Keywords: X-ray structures; Niobium; Tantalum; Dinuclear complexes

1. Introduction

Considerable interest has focussed on the synthesis and chemistry of binuclear complexes containing two different transition metals [1]. For example, phosphido-bridged [2,3], oxo-bridged [4] or thiolato-bridged [5] heterobimetallic complexes have received particular attention. One reason for interest in such species is the possibility that new reactivity patterns will emerge, which might be substantially different from those of binuclear complexes containing a direct metal–metal bond.

In view of the interesting functionalized transition metal complexes with niobium or tantalum, we decided to investigate the synthesis and chemical reactivity of compounds containing the grouping PR_2X ($\text{X} = \text{O}$ or S) and their application in the preparation of new bimetallic $\text{M-P-X-M}'$ systems ($\text{M} = \text{Nb}$ or Ta ; $\text{X} = \text{O}$

or S). In this paper, we report the isolation, detailed structural characterization, and reactivity towards organic and organometallic electrophilic reagents of $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2\text{X})]$ ($\text{M} = \text{Nb}$ or Ta ; $\text{R} = \text{Me}$ or Ph ; $\text{X} = \text{O}$ or S). The initial results in this field have been previously reported in a short communication [6].

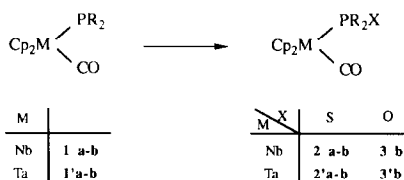
2. Results and discussion

2.1. $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2\text{O})]$ and $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2\text{S})]$

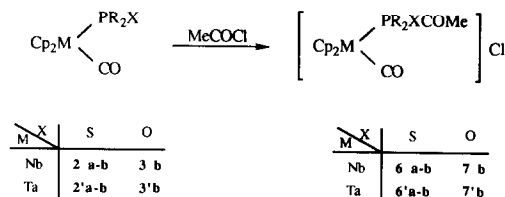
Complexes **1a**, **1b**, **1'a** and **1'b** [7] can be easily converted into the corresponding oxides or sulfides by treatment of their toluene solutions with hydrogen peroxide and elemental sulfur respectively (Scheme 1).

The sulfur complexes are obtained as cream crystals and the corresponding oxygen complexes as pink crystalline solids. Unlike **2a** (or **2'a**) the dimethyl oxygen derivatives cannot be isolated. Their spectroscopic data are consistent with the structures proposed for **2** and **3**. The IR spectra exhibit $\text{P}=\text{O}$ (at 1033 cm^{-1} for **3b**) or

* Corresponding author.



Scheme 1. a, R = Me; b, R = Ph.



Scheme 3.

P=S (at 570 cm^{-1} for **2b**) bands. The $\{^1\text{H}\} ^{31}\text{P}$ NMR data show a deshielded signal when compared with their precursor complexes (about 110 ppm in **2a** and about 80 ppm in **2b**).

2.2. Reactivity of phosphoramido complexes towards organic electrophilic reagents

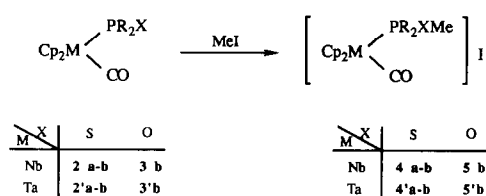
Stirring toluene solutions of **2** or **3** and methyl iodide at room temperature forms orange salts **4** or **5** in an almost quantitative yield (Scheme 2).

Under the same conditions, reaction with acetyl chloride affords yellow precipitates of the corresponding salts **6** or **7**. The spectroscopic data are consistent with products resulting from an electrophilic attack at the electron-rich oxygen and sulfur atoms respectively and not at the nucleophilic d^2 transition metal (Scheme 3).

The methylation and acylation at the sulfur atom are responsible for a moderately deshielded ^{31}P NMR signal when compared with that of the corresponding thiodiphenylphosphoramido complexes (about 10 ppm for **4b** or **4' b** and about 20 ppm for **6b** or **6' b**). This deshielding effect is more pronounced in the thiodimethylphosphoramido complexes (about 20 ppm for **4a** or **4' a** and about 40 ppm for **6a** or **6' a**) and the oxodiphenylphosphoramido complexes (69 ppm for **5b** and 79 ppm for **7b**).

IR spectral data for these complexes show that $\nu(\text{P}=\text{S})$ decreases (about 40 cm^{-1}) on methylation, consistent with bonding of the methyl group to the sulfur atom. Moreover, methylation or acylation leads to a high frequency $\nu(\text{CO})$: 1938 cm^{-1} in **2a**, 1964 cm^{-1} in **4a**, and 1959 cm^{-1} in **6a**.

In order to confirm the site of the electrophilic attack, the structure of the methyl complex $[\text{Cp}_2\text{Nb}(\text{CO})(\text{PPh}_2\text{SMe})]\text{I}$ (**4b**) has been determined by single-crystal X-ray diffraction. Comparison of the structure



Scheme 2.

of **4b** with that of the related bimetallic complex $[\text{Cp}_2\text{Ta}(\text{CO})(\mu, \eta^1: \eta^1\text{-PMe}_2\text{S})\text{W}(\text{CO})_5]$ will be discussed later.

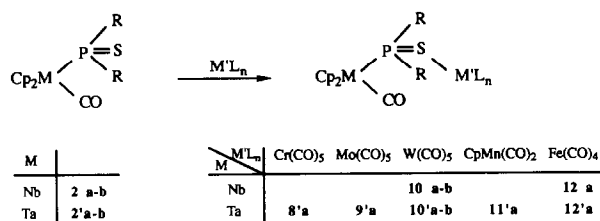
2.3. Reactivity of thiophosphoramido complexes towards organometallic electrophilic reagents

In contrast to the oxo derivatives, the sulfide compounds **2a** and **2' a** react readily with $[\text{Fe}_2(\text{CO})_9]$ or with unsaturated organometallic species such as $\text{Cr}(\text{CO})_5$, $\text{Mo}(\text{CO})_5$, $\text{W}(\text{CO})_5$ and $\text{CpMn}(\text{CO})_2$ to give bimetallic complexes incorporating a Group 6, 7 or 8 metal (Scheme 4). In the same manner, phenyl compounds **2b** and **2' b** lead to dinuclear complexes containing Nb or Ta, and W (**10b** and **10' b**).

These compounds are characterized by field desorption mass spectrometry. Coordination at the sulfur is inferred from the IR, ^1H , NMR and ^{31}P NMR data and furthermore confirmed by the X-ray analysis for complex **10' a**. A ^{31}P signal moderately deshielded by comparison with that of the precursor (18 ppm when R = Me and 12 ppm when R = Ph) is also observed. Additional information on structures is provided by an analysis of the IR spectra in the $\nu(\text{P}=\text{S})$ region. $\nu(\text{P}=\text{S})$ appears to have decreased (30 cm^{-1} approximately) on coordination. These data are similar to those obtained for $[(\text{R}_3\text{PS})\text{Cr}(\text{CO})_5]$ [8] and confirm the presence of a sulfur–metal bonds in these bimetallic complexes.

2.4. Molecular structure of **4b** and **10' a**

ORTEP drawings of the cation $[\text{Cp}_2\text{Nb}(\text{CO})(\text{PPh}_2\text{SMe})]$ in **4b** and of the molecule $[\text{Cp}_2\text{Ta}(\text{CO})(\mu, \eta^1: \eta^1\text{-PMe}_2\text{S})\text{W}(\text{CO})_5]$ (**10' a**) are shown in Figs. 1 and 2 respectively. The principal bond lengths and bond angles are given in Table 1.



Scheme 4.

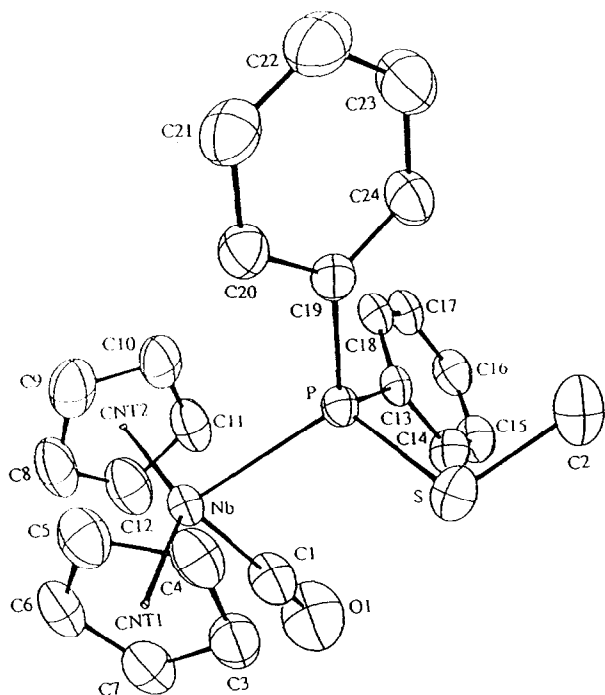


Fig. 1.

In both structures the various fragments have typical geometries, *i.e.* distorted tetrahedral for the metallocene part and octahedral for the tungsten atom in the carbonyl moiety. The metal–phosphorus bond lengths are essentially the same in **4b** (2.579(1) Å) and in **10'a** (2.572(6) Å). They are, however, shorter than the M–P distances in complex [Cp₂Nb(CO)(PPh¹Pr)] (**I**) (2.631(5) Å) [9], which has a terminal pyramidal phosphide, and in the monophosphido-bridged complex [(C₅Me₅)(C₅H₅)Ta(CO)(μ-PPh₂)Mn(CO)₂(C₅H₅)] (**II**) (2.708(2) Å) [10]. Comparison of the niobocene

Table 1

Principal bond lengths (Å) and bond angles (°) for [(C₅H₅)₂Nb(CO)(PPh₂SMe)] (**4b**) and [(C₅H₅)₂Ta(CO)(μ, η¹: η¹-PMe₂S)W(CO)₅] (**10'a**)

	4b	10'a
Bond lengths		
Ta...W		6.29
M–P	2.579(1)	2.572(6)
M–C(CO)	2.058(4)	1.97(2)
M–CNT(1)	2.055	2.067
M–CNT(2)	2.052	2.072
C–O(MCO)	1.140(5)	1.20(3)
P–S	2.092(1)	2.049(8)
S–C(2)(Me)	1.806(4)	
S–W		2.599(6)
W–C(1)		2.09(3)
W–C(2)		1.97(3)
W–C(3)		1.96(2)
W–C(4)		2.19(3)
W–C(5)		1.93(2)
Bond angles		
P–M–C(CO)	86.2(1)	88.3(8)
CNT(1)–M–CNT(2)	137.9	138.7
M–C–O	177.7(3)	174(2)
M–P–S	110.1(2)	113.7(3)
P–S–C(2)(Me)	103.7(1)	
P–S–W		114.6(3)

CNT(1) and CNT(2) are the centres of gravity of the C(3)–C(7), and C(8)–C(12) rings respectively in **4b** and the C(11)–C(15) and C(16)–C(20) rings respectively in **10'a**.

and tantalocene complexes is justified because the covalent radii of Nb and Ta differ only by 0.01 Å [11a] owing to the lanthanide contraction. The shorter bonds observed in complexes **4b** and **10'a** may be attributed primarily to the presence of formally smaller P(V) instead of P(III) in **I** and **II**. However, this is probably not a fully satisfactory explanation for various reasons.

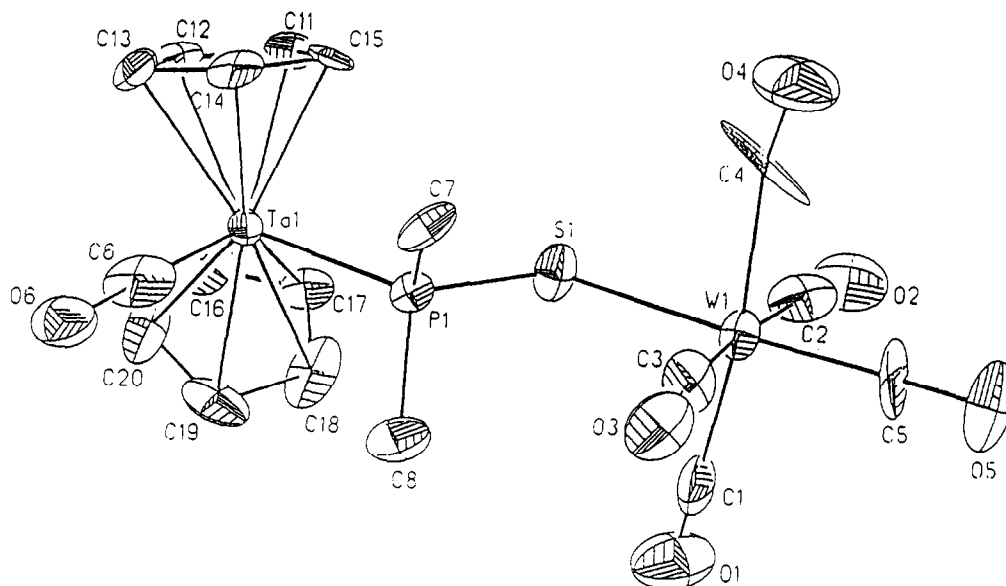
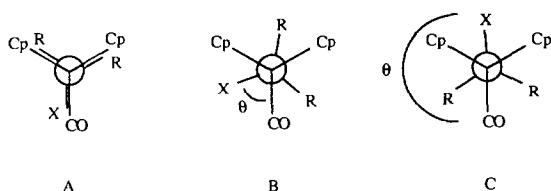


Fig. 2.

The distances observed in **4b** and **10'a** correspond very well with the Nb–P(phosphine) bond length (2.565(15) Å) reported for [CpNb(PPh₃)(CO)(H₂)] [12]. The Nb–P bond in **I** is long because of the repulsions between the lone pairs localized on niobium and on phosphorus. This is consistent with a general statement that the metal–P (terminal pyramidal phosphide) bonds are longer than the metal–P(phosphine) bonds [13,14]. Even if the ‘transition metal *gauche* effect’ [9,15] (adoption of a geometry in which the total energy and the repulsions between lone pairs) is minimized, the metal–phosphide bonds remain long. However, the phosphorus lone pair in **II** is involved in the bonding with a second metal fragment, but steric repulsions between this fragment and the metallocene part of the molecule are responsible for the long M–P distance observed in **II**. A very long Mo–P bond (2.602(2) Å) has also been found in the analogous structure [Cp₂Mo(H)(μ-PPh₂)Mn(CO)₂Cp] (**III**) [3]. Strong steric repulsions between the metal fragments in **II** and in **III** is supported by the extremely large M–P–M' angles observed (125.5(1)° and 124.5(1)° respectively), as well as in [(C₅Me₄Et)(C₅H₅)Ta(CO)(μ-PPh(OMe))]Cr(CO)₅] (127.1(1)°) [16]. In **4b** and **10'a** the coordination site corresponding to the phosphorus lone pair in **I** is occupied by sulfur atom and steric constraints because bulky W(CO)₅ fragment no longer exist in **10'a**. This fragment is remoted from the Cp₂M(CO)(PR₂) fragment by the sulfur atom. Consequently, the M(Nb,Ta)–P–S angles of 110.1(2)° in **4b** (close to the ideal tetrahedral value) and 113.7(3)° in **10'a** are much smaller than the M–P–M' angles observed in the monophosphido-bridged complexes **II** and **III**, and the M–P distances become shorter.

Three possible orientations of Cp₂M(CO, H)(PR₂X) systems (depicted in Scheme 5) are of value for the comparison of the geometries found in **4b** and **10'a** with those observed in **I–III**.

The structure A has never been observed in monophosphido-bridged binuclear complexes derived from metallocenes of Groups 5 and 6 metals in the absence of metal–metal bonds and of other bridges. In the terminal phosphide complex **I**, this structure is a consequence of the ‘*gauche* effect’ and in **II** and **III** bearing a diphenylphosphido bridge it is probably due to the steric repulsions between metal fragments. The dihedral angles (CO,H)MP–MPX are 74° for **I** (X is



Scheme 5.

the phosphorus lone pair), 69.3° for **II**, 68.2° for **III** and 69.4° for **4b** and correspond to conformation B. Conformation C has been observed for the first time in the structure of **10'a** in which the (CO)TaP–TaPS angle is 175.8°. This inversion of positions of the R groups attached to phosphorus with respect to the Cp₂M(CO) fragment may be due to the smaller size of methyl substituents compared with phenyl. Such an *endo* orientation of Me groups with respect to the CO compels them to occupy symmetrically positions on each side of the (CO)TaP plane bisecting that of Cp rings. Consequently, the C(6), Ta, P and S atoms (Fig. 2) should be coplanar, as observed. This suggests electron delocalization over these atoms.

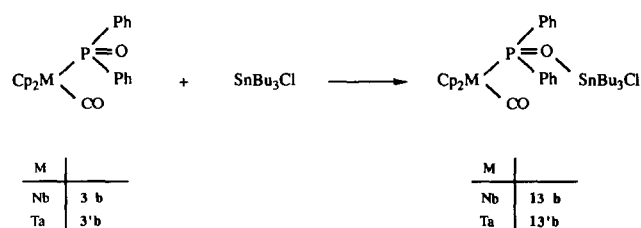
Such a delocalization should decrease the double-bond character of the P=S bond in **10'a** and probably increase the electron density on the Cp₂Ta(CO) fragment. This seems to be confirmed by a shorter Ta–C(6)(CO) bond length (1.97(2) Å) than the M–C(CO) distances observed in **II** (2.03(2) Å) [10] and in **4b** (2.058(4) Å, Table 1). A shortening of the M–CO bond is due to stronger M → CO π back bonding. The P–S bond length in **10'a** is essentially the same as that in the Mo(V) complex [MoCl₃O(SPPH₃)] (2.041(1) Å) [17], but significantly longer than in [Cr(CO)₅(SPMe₃)] (1.990(3) Å) [18]. The Cr–S bond of 2.510(2) Å in this last compound is very long and, because of the difference between the covalent radii of Cr and W (0.14 Å [11b]), must be considered to be much weaker than the W–S bond in **10'a** (2.599(6) Å). Thus, the double-character of the phosphorus–sulfur bond is weaker in **10'a** than in the chromium complex. For comparison, we note that the P=S bond lengths in phosphine sulfides are in the range 1.94–1.96 Å [19,20].

Finally, from a crystallochemical point of view, the difference between the P–S bond lengths in P–S–C (2.092(1) Å, **4b**) and in P–S–M (2.049(8) Å, **10'a**; 2.041(1) Å, [MoCl₃O(SPPH₃)] [17]) bond lengths is consistent with the observations made for phosphates with P–O–C and P–O–M bonds [21]. The mean values of ‘bridging’ P–O bond lengths are close to 1.59 Å in structures of the type O₂P(OC)₂ and to 1.61 Å in the O₃P(OC) types with covalent carbon–oxygen bonding. They are close to 1.55 Å in compounds with the O₂P(OM)₂ unit, where weaker and less covalent metal–oxygen interactions are present.

2.5. Reactivity of oxophosphoramides towards Bu₃SnCl

In an attempt to synthesize another type of hetero-bimetallic system with a new Nb(Ta)–P–O–M' core, we have mixed the oxophosphoramides complexes with tin(IV) compounds such as Bu₃SnCl (Scheme 6).

The resulting reaction products have been formulated as five-coordinated organotin binuclear complexes [22]. The ³¹P NMR spectra of **13b** and **13'b**



Scheme 6.

show a moderately deshielded signal compared with **3b** and **3'b** (23 ppm and 18 ppm respectively).

In contrast, the thiophosphoramides do not react with these tin(IV) compounds, consistent with the soft character of the coordination site.

In conclusion, we have synthesized a new class of metalloligands able to react with organic electrophilic species or to link organometallic fragments via a P–S or a P–O bridge; the phosphine oxides bind exclusively “hard” metallic elements whereas sulfides associate “soft” Group 6, 7 and 8 metal carbonyl fragments. Further work is in progress to investigate the reactivities of these new precursors of bimetallic complexes.

3. Experimental section

3.1. Materials and methods

All preparative reactions were performed under argon. Tetrahydrofuran (THF), toluene and pentane were distilled from sodium benzophenone ketyl. Phosphido complexes $\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2)$ [7] and $[\text{M}(\text{CO})_5(\text{THF})]$ [23] were prepared by published procedures. Column chromatography was carried out on silica gel (70–230 mesh). The following instruments were used in this work: Nicolet 205 (IR); Bruker AC 200 (^1H and ^{31}P NMR). Field desorption mass spectra were run on a Finnigan MAT 311 A instrument from toluene, acetone and chloroform solutions. Elemental analyses were performed by the CNRS microanalytical laboratory.

3.2. Syntheses of the new complexes

3.2.1. $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2\text{S})]$ (**2a**, **2b**; **2a'**, **2'b**)

A 61 mg (0.24 mmol) sample of elemental sulfur was added to a solution of 200 mg (0.64 mmol) of **1a** [$\text{Cp}_2\text{Nb}(\text{CO})(\text{PMe}_2)$] in 20 ml of toluene. After 5 min, the solvent of the pink mixture was removed under vacuum. The crude reaction product was chromatographed on silica gel with THF as eluant. Complex **2a** [$\text{Cp}_2\text{Nb}(\text{CO})(\text{PMe}_2\text{S})$] was obtained with a 74% yield

[Cp₂Nb(CO)(PMe₂S)] (2a): IR (CsI): $\nu(\text{P}=\text{S})$ 546 cm^{-1} . IR (CHCl_3): $\nu(\text{CO})$ 1938 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1929 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 5.43 (d, $J = 2.2$

Hz, Cp); 1.60 (d, $J = 8$ Hz, Me). ^{31}P NMR (CD_3COCD_3): δ 42 (s).

Compounds **2b** and **2'a**, **2'b** were prepared similarly with a 70–75% yield.

[Cp₂Nb(CO)(PPh₂S)] (2b): Anal. Found: C, 59.3; H, 4.1. $\text{C}_{23}\text{H}_{20}\text{NbOPS}$ calc.: C, 59.0; H, 4.3%. Field desorption mass spectroscopy (FDMS) (toluene): 440.2 ($\text{M}^+ - \text{CO}$). IR (CsI): $\nu(\text{P}=\text{S})$ 570 cm^{-1} . IR (CHCl_3): $\nu(\text{CO})$ 1928 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1917 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 8.20–7.15 (m, Ph); 5.24 (d, $J = 2.2$ Hz, Cp). ^{31}P NMR (CD_3COCD_3): δ 75 (s).

[Cp₂Ta(CO)(PMe₂S)] (2'a): Anal. Found: C, 37.0; H, 3.4. $\text{C}_{13}\text{H}_{16}\text{OPSTa}$ calc.: C, 36.1, H, 3.7%. IR (CsI): $\nu(\text{P}=\text{S})$ 554 cm^{-1} . IR (CHCl_3): $\nu(\text{CO})$ 1924 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1912 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 5.39 (d, $J = 2.2$ Hz, Cp); 1.67 (d, $J = 8$ Hz, Me). ^{31}P NMR (CD_3COCD_3): δ 15 (s).

[Cp₂Ta(CO)(PPh₂S)] (2'b): FDMS (toluene): 528.4 ($\text{M}^+ - \text{CO}$). IR (CsI): $\nu(\text{P}=\text{S})$ 574 cm^{-1} . IR (CHCl_3): $\nu(\text{CO})$ 1912 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1905 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 8.20–7.20 (m, Ph); 5.20 (d, $J = 2.2$ Hz, Cp). ^{31}P NMR (CD_3COCD_3): δ 52 (s).

3.2.2. $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2\text{O})]$ (**3b**; **3'b**)

To a stirred solution of 270 mg of **1b** [$\text{Cp}_2\text{Nb}(\text{CO})(\text{PPh}_2)$] (0.62 mmol) in 15 ml of toluene was added 0.9 ml of H_2O_2 (3%) followed by 5 ml of $\text{Na}_2\text{S}_2\text{O}_3$ (10%). A color change from brown to pink was observed accompanied by the formation of a precipitate. The mixture was filtered and the precipitate was washed with toluene and pentane. After the solvent was removed, **3b** [$\text{Cp}_2\text{Nb}(\text{CO})(\text{PPh}_2\text{O})$] was obtained with a 80% yield.

[Cp₂Nb(CO)(PPh₂O)] (3b): Anal. Found: C 61.9, H, 4.1. $\text{C}_{23}\text{H}_{20}\text{NbO}_2\text{P}$ calc.: C, 61.1; H, 4.4%. FDMS (acetone): 424.1 ($\text{M}^+ - \text{CO}$). IR (CsI): $\nu(\text{P}=\text{O})$ 1033 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1919 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 8.00–7.20 (m, Ph); 5.21 (d, $J = 2.2$ Hz, Cp). ^{31}P NMR (CD_3COCD_3): δ 98 (s).

[Cp₂Ta(CO)(PPh₂O)] (3'b): FDMS (acetone): 512.2 ($\text{M}^+ - \text{CO}$). IR (CsI): $\nu(\text{P}=\text{O})$ 1029 cm^{-1} , IR (CHCl_3): $\nu(\text{CO})$ 1928 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1905 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 7.90–7.20 (m, Ph); 5.18 (d, $J = 2.2$ Hz, Cp). ^{31}P NMR (CD_3COCD_3): δ 77 (s).

3.2.3. $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2\text{XMe})]$ (**4a**, **4b**; **4'a**, **4'b**; **5b**; **5'b**)

A solution of 200 mg (0.58 mmol) of **2a** [$\text{Cp}_2\text{Nb}(\text{CO})(\text{PMe}_2\text{S})$] in 20 ml of toluene was treated with one equivalent of MeI. This afforded an orange

precipitate. After filtration, product **4a** was washed with toluene and pentane and was dried under vacuum. It was obtained in quantitative yield.

[Cp₂Nb(CO)(PMe₂SMe)]I (4a): IR (CsI): $\nu(\text{P}=\text{S})$ 501 cm^{-1} . IR (CHCl₃): $\nu(\text{CO})$ 1964 cm^{-1} . ¹H NMR (CDCl₃): δ 5.64 (d, $J = 2.2$ Hz, Cp); 2.24 (d, $J = 9$ Hz, SMe); 1.9 (d, $J = 7$ Hz, PMe₂). ³¹P NMR (CDCl₃): δ 62 (s).

Compounds **4b** and **4'a**, **4'b** were prepared similarly and obtained with the same yield.

[Cp₂Nb(CO)(PPh₂SMe)]I (4b): Anal. Found: C, 47.0; H, 3.8. C₂₄H₂₃INbOPS calc.: C, 47.2; H, 3.8%. FDMS (CHCl₃): 483.3 (M⁺). IR (CsI): $\nu(\text{P}=\text{S})$ 522 cm^{-1} . IR (CHCl₃): $\nu(\text{CO})$ 1966 cm^{-1} . ¹H NMR (CDCl₃): δ 7.70–7.40 (m, Ph); 5.55 (d, $J = 2$ Hz, Cp); 2.10 (d, $J = 8$ Hz, SMe). ³¹P NMR (CDCl₃): δ 81 (s).

[Cp₂Ta(CO)(PMe₂SMe)]I (4'a): Anal. Found: C, 29.9; H, 3.2. C₁₄H₁₉IOPSTa calc.: C, 29.3; H, 3.3%. IR (CsI): $\nu(\text{P}=\text{S})$ 503 cm^{-1} . IR (CHCl₃): $\nu(\text{CO})$ 1950 cm^{-1} . ¹H NMR (CDCl₃): δ 5.60 (d, $J = 2.4$ Hz, Cp); 2.22 (d, $J = 9.5$ Hz, SMe); 1.96 (d, $J = 7$ Hz, PMe₂). ³¹P NMR (CDCl₃): δ 31 (s).

[Cp₂Ta(CO)(PPh₂SMe)]I (4'b): Anal. Found: C, 42.2; H, 3.5. C₂₄H₂₃IOPSTa calc.: C, 41.3; H, 3.3%. IR (CsI): $\nu(\text{P}=\text{S})$ 529 cm^{-1} . IR (CHCl₃): $\nu(\text{CO})$ 1951 cm^{-1} . ¹H NMR (CDCl₃): δ 7.60–7.50 (m, Ph); 5.37 (d, $J = 2.2$ Hz, Cp); 2.05 (d, $J = 9$ Hz, SMe). ³¹P NMR (CDCl₃): δ 54 (s).

Compounds **5b** and **5'b** may be made by an analogous procedure with THF instead of toluene.

[Cp₂Nb(CO)(PPh₂OMe)]I (5b): IR (THF): $\nu(\text{CO})$ 1939 cm^{-1} . ¹H NMR (CDCl₃): δ 7.65–7.55 (m, Ph); 5.49 (d, $J = 2$ Hz, Cp); 3.59 (d, $J = 11$ Hz, OMe). ³¹P NMR (CDCl₃): δ 167 (s).

[Cp₂Ta(CO)(PPh₂OMe)]I (5'b): IR (THF): $\nu(\text{CO})$ 1924 cm^{-1} . ¹H NMR (CDCl₃): δ 7.65–7.55 (m, Ph); 5.45 (d, $J = 2$ Hz, Cp); 3.63 (d, $J = 12$ Hz, OMe). ³¹P NMR (CDCl₃): δ 142 (s).

3.2.4. [Cp₂M(CO)(PR₂XCOMe)]Cl (**6a**, **6b**; **6'a**, **6'b**; **7b**; **7'b**)

To a solution of 200 mg (0.58 mmol) of **2a** [Cp₂Nb(CO)(PMe₂S)] in 20 ml of toluene was added one equivalent of MeCOCl. The yellow precipitate was filtered, washed with toluene and pentane and dried under vacuum. Product **6a** was obtained with a quantitative yield.

[Cp₂Nb(CO)(PMe₂SCOMe)]Cl (6a): Anal. Found: C, 42.1; H, 4.8. C₁₅H₁₉ClINbO₂PS calc.: C, 42.6; H, 4.5%. IR (CHCl₃): $\nu(\text{CO})$ 1959–1930 cm^{-1} . ¹H NMR (CDCl₃): δ 5.65 (d, $J = 2.2$ Hz, Cp); 2.37 (d, $J = 1$ Hz, COMe); 2.08 (d, $J = 7$ Hz, PMe₂). ³¹P NMR (CDCl₃): δ 79 (s).

Compounds **6b**, **6'a**, **6'b**, **7b** and **7'b** were prepared by an analogous procedure and obtained in the same yield.

[Cp₂Nb(CO)(PPh₂SCOMe)]Cl (6b): IR (CHCl₃): $\nu(\text{CO})$ 1964, 1931 cm^{-1} . ¹H NMR (CDCl₃): δ 7.60–7.50 (m, Ph); 5.56 (d, $J = 2$ Hz, Cp); 2.43 (d, $J = 1$ Hz, COMe). ³¹P NMR (CDCl₃): δ 91 (s).

[Cp₂Ta(CO)(PMe₂SCOMe)]Cl (6'a): IR (CHCl₃): $\nu(\text{CO})$ 1948, 1729 cm^{-1} . ¹H NMR (CDCl₃): δ 5.64 (d, $J = 2.2$ Hz, Cp); 2.38 (d, $J = 1$ Hz, COMe); 2.19 (d, $J = 8$ Hz, PMe₂). ³¹P NMR (CDCl₃): δ 49 (s).

[Cp₂Ta(CO)(PPh₂SCOMe)]Cl (6'b): IR (CHCl₃): $\nu(\text{CO})$ 1951, 1735 cm^{-1} . ¹H NMR (CDCl₃): δ 7.60–7.50 (m, Ph); 5.53 (d, $J = 2.2$ Hz, Cp); 2.44 (d, $J = 1$ Hz, COMe). ³¹P NMR (CDCl₃): δ 64 (s).

[Cp₂Nb(CO)(PPh₂OCOMe)]Cl (7b): ¹H NMR (CD₃COCD₃): δ 7.80–7.50 (m, Ph); 5.71 (d, $J = 2.2$ Hz, Cp); 2.52 (d, $J = 1$ Hz, COMe). ³¹P NMR (CD₃COCD₃): δ 177 (s).

[Cp₂Ta(CO)(PPh₂OCOMe)]Cl (7'b): IR (CHCl₃): $\nu(\text{CO})$ 1940, 1701 cm^{-1} . ¹H NMR (CD₃COCD₃): δ 7.80–7.50 (m, Ph); 5.66 (d, $J = 2.2$ Hz, Cp); 2.55 (d, $J = 1$ Hz, COMe). ³¹P NMR (CD₃COCD₃): δ 150 (s).

3.2.5. [Cp₂M(CO)(μ , η^1 : η^1 -PR₂S)M'(CO)₅] (**8'a**; **9'a**; **10a**, **10b**; **10'a**, **10'b**)

To a solution of 250 mg (0.58 mmol) of [Cp₂Ta(CO)(PMe₂S)] (**2'a**) in 15 ml of THF was added an excess of [Cr(CO)₅(THF)]. The mixture was stirred for 15 min at room temperature (the reaction was monitored by IR spectroscopy). The solvent was removed under vacuum and the crude reaction product was chromatographed on silica gel with THF:toluene (10:100) as eluant. The bimetallic complex **8'a** [Cp₂Ta(CO)(μ , η^1 : η^1 -PMe₂S)Cr(CO)₅] was obtained with a 55% yield.

[Cp₂Ta(CO)(μ , η^1 : η^1 -PMe₂S)Cr(CO)₅] 8'a: Anal. Found: C, 34.9; H, 2.8; C₁₈H₁₆CrO₆PSTa calc.: C, 34.6; H, 2.6%. FDMS (acetone): 624.0 (M⁺). IR (CsI): $\nu(\text{P}=\text{S})$ 507 cm^{-1} . IR (THF): $\nu(\text{CO})$ 2046, 1929, 1912, 1881 cm^{-1} . ¹H NMR (CD₃COCD₃): δ 5.51 (d, $J = 2$ Hz, Cp); 1.85 (d, $J = 8$ Hz, Me). ³¹P NMR (CD₃COCD₃): δ 30 (s).

Compounds **9'a**, **10a**, **10b** and **10'a**, **10'b** were prepared similarly with a 50–60% yield.

[Cp₂Ta(CO)(μ, η¹: η¹-PMe₂S)Mo(CO)₅] (9'a): FDMS (acetone): 670.0 (M⁺). IR (CsI): ν(P=S) 515 cm⁻¹. IR (THF): ν(CO) 2061, 1931, 1922, 1880 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 5.51 (d, *J* = 2 Hz, Cp); 1.82 (d, *J* = 8 Hz, Me). ³¹P NMR (CD₃COCD₃): δ 26 (s).

[Cp₂Nb(CO)(μ, η¹: η¹-PMe₂S)W(CO)₅] (10a): IR (CsI): ν(P=S) 511 cm⁻¹. IR (THF): ν(CO) 2050, 1923, 1910, 1876 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 5.57 (d, *J* = 2.2 Hz, Cp); 1.73 (d, *J* = 7.5 Hz, Me). ³¹P NMR (CD₃COCD₃): δ 58 (s).

[Cp₂Nb(CO)(μ, η¹: η¹-PPh₂S)W(CO)₅] (10b): IR (CsI): ν(P=S) 535 cm⁻¹. IR (THF): ν(CO) 2060, 1923, 1875 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.80–7.45 (m, Ph); 5.38 (d, *J* = 2.2 Hz, Cp). ³¹P NMR (CD₃COCD₃): δ 84 (s).

[Cp₂Ta(CO)(μ, η¹: η¹-PMe₂S)W(CO)₅] (10'a): Anal. Found: C, 28.7; H, 2.3; C₁₈H₁₆O₆PSTaW calc.: C, 28.6;

H, 2.1%. IR (CsI): ν(P=S) 515 cm⁻¹. IR (THF): ν(CO) 2058, 1924, 1911, 1870 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 5.53 (d, *J* = 2.2 Hz, Cp); 1.82 (d, *J* = 8 Hz, Me). ³¹P NMR (CD₃COCD₃): δ 28 (s).

[Cp₂Ta(CO)(μ, η¹: η¹-PPh₂S)W(CO)₅] (10'b): FDMS (acetone): 880.5 (M⁺). IR (CsI): ν(P=S) 539 cm⁻¹. IR (THF): ν(CO) 2060, 1940, 1922, 1875 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.80–7.45 (m, Ph); 5.34 (d, *J* = 2 Hz, Cp). ³¹P NMR (CD₃COCD₃): δ 58 (s).

3.2.6. **[Cp₂Ta(CO)(μ, η¹: η¹-PMe₂S)Mn(Cp(CO))₂] (11'a)**

This compound was prepared by an analogous procedure to **8'a** with a 45% yield.

[Cp₂Ta(CO)(μ, η¹: η¹-PMe₂S)Mn(Cp(CO))₂] (11'a): Anal. Found: C, 40.1; H, 3.1. C₂₀H₂₁MnO₃PSTa calc.: C, 39.5; H, 3.5%. IR (CsI): ν(P=S) 511 cm⁻¹. IR (THF): ν(CO) 1922, 1905, 1833 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 5.42 (d, *J* = 2 Hz, Cp₂Ta); 4.30 (s, CpMn), 1.72 (d, *J* = 8 Hz, Me). ³¹P NMR (CD₃COCD₃): δ 30 (s).

Table 2

Crystallographic and Experimental Data for [(C₅H₅)₂Nb(CO)(PPh₂SMe)]I (**4b**) and (C₅H₅)₂Ta(CO)(μ, η¹: η¹-PMe₂S)W(CO)₅ (**10'a**)

	4b	10'a
Chemical formula	C ₂₄ H ₂₃ INbOPS	C ₁₈ H ₁₆ O ₆ PSTaW
Formula weight	630.46	669.19
Color	Orange	Red
Crystal system	Triclinic	Monoclinic
Space group	P1	P2 ₁ /n
<i>a</i> (Å)	9.875(2)	7.849(5)
<i>b</i> (Å)	10.756(2)	21.78(2)
<i>c</i> (Å)	11.566(3)	12.94(1)
α (°)	87.56(2)	
β (°)	76.75(2)	99.36(6)
γ (°)	82.35(2)	
<i>v</i> (Å ³)	1185.0	2182.7
<i>Z</i>	2	4
ρ _{calc} (g cm ⁻³)	1.767	2.30
<i>F</i> (000)	640	1400
μ(Mo Kα) (cm ⁻¹)	19.412	105.3
Radiation	Mo Kα; λ = 0.71073 Å	Mo Kα; λ = 0.71068 Å
Temperature (K)	295	295
Scan type	ω-2θ	ω-θ
<i>hkl</i>		
lower limit	-11, -12, 0	-11, 0, 0
upper limit	11, 12, 13	11, 30, 18
θ range (°)	2–25	1.5–30
linear decay (%)	-1.3 (corrected)	
Total number of reflections	4519	6615
Number of unique reflections	3435 (<i>I</i> > 3σ(<i>I</i>))	3813 (<i>I</i> > 3σ(<i>I</i>))
Number of variables	262	254
Absorption correction, Ψ scan	0.964–0.999	0.23–1.0
<i>R</i>	0.026	0.067
<i>R</i> _w	0.025	0.057
Goodness of fit	3.894	3.08
Weighting scheme	w = 1/σ ² (<i>F</i>)	
Residual density (electrons Å ⁻³)	+0.25 to -0.40	+3.45 to -3.61

3.2.7. $[\text{Cp}_2\text{M}(\text{CO})(\mu, \eta^1: \eta^1\text{-PMe}_2\text{S})\text{Fe}(\text{CO})_4]$ (**12a**, **12'a**)

Equimolar amounts of $[\text{Cp}_2\text{Ta}(\text{CO})(\text{PMe}_2\text{S})]$ (**2'a**) and $[\text{Fe}_2(\text{CO})_9]$ in 20 ml of THF were stirred at room temperature. The progress of the reaction was monitored by recording IR spectra. After 1 h, the solvent of the dark-brown mixture was removed under vacuum and the residue was chromatographed on silica gel with toluene as eluant. The orange complex **12'a** was obtained with a 40% yield.

$[\text{Cp}_2\text{Ta}(\text{CO})(\mu, \eta^1: \eta^1\text{-PMe}_2\text{S})\text{Fe}(\text{CO})_4]$ (12'a**):** FDMS (acetone): 600.5 (M^+). IR (CsI): $\nu(\text{P}=\text{S})$ 504 cm^{-1} . IR (THF): $\nu(\text{CO})$ 2022, 1946, 1926, 1909 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 5.53 (d, $J = 2$ Hz, Cp); 1.82 (d, $J = 8$ Hz, Me). ^{31}P NMR (CD_3COCD_3): δ 30 (s).

Compound **12a** was prepared similarly with the same yield.

Table 3

Atomic coordinates and equivalent isotropic displacement parameters for $[(\text{C}_5\text{H}_5)_2\text{Nb}(\text{CO})(\text{PPh}_2\text{SMe})]\text{I}$ (**4b**)

Atom	x	y	z	U_{eq}^1 (\AA^2)
I	0.67905(3)	0.20906(3)	0.91699(2)	67(1)
Nb	0.14391(3)	0.27585(3)	0.23799(3)	31(1)
S	-0.13283(9)	0.21275(8)	0.51884(7)	41(1)
P	-0.10414(8)	0.22231(7)	0.33396(7)	28(1)
C(1)	0.0759(4)	0.4506(4)	0.3109(4)	56(2)
O(1)	0.0416(4)	0.5490(3)	0.3484(3)	95(3)
CNT(1)	0.2800	0.1923	0.3370	
CNT(2)	0.1420	0.3063	0.0620	
C(2)	-0.3160(4)	0.1938(4)	0.5704(3)	50(2)
C(3)	0.2063(4)	0.2445(4)	0.4236(3)	50(2)
C(4)	0.1982(4)	0.1229(3)	0.3851(3)	45(2)
C(5)	0.3010(4)	0.0980(3)	0.2799(3)	49(2)
C(6)	0.3758(4)	0.2036(4)	0.2541(3)	49(2)
C(7)	0.3190(4)	0.2928(4)	0.3422(3)	55(2)
C(8)	0.2664(5)	0.2954(5)	0.0378(3)	68(3)
C(9)	0.1843(5)	0.1978(5)	0.0402(3)	64(3)
C(10)	0.0425(4)	0.2507(4)	0.0715(3)	56(2)
C(11)	0.0387(4)	0.3799(4)	0.0915(3)	56(2)
C(12)	0.1783(5)	0.4075(5)	0.0688(4)	68(3)
C(13)	-0.2408(3)	0.3464(3)	0.3089(3)	29(2)
C(14)	-0.2764(4)	0.4503(3)	0.3830(3)	39(2)
C(15)	-0.3690(4)	0.5509(3)	0.3585(3)	47(2)
C(16)	-0.4265(4)	0.5490(3)	0.2610(4)	48(2)
C(17)	-0.3921(3)	0.4463(3)	0.1872(3)	43(2)
C(18)	-0.2996(3)	0.3442(3)	0.2115(3)	36(2)
C(19)	-0.1576(3)	0.0761(3)	0.2962(3)	23(2)
C(20)	-0.0530(4)	-0.0224(3)	0.2566(3)	41(2)
C(21)	-0.0881(4)	-0.1396(3)	0.2343(3)	49(2)
C(22)	-0.2260(5)	-0.1566(4)	0.2504(3)	55(2)
C(23)	-0.3305(4)	-0.0595(4)	0.2874(4)	57(3)
C(24)	-0.2969(4)	0.0568(3)	0.3116(3)	44(2)

CNT(1) and CNT(2) are the gravity centers of the C(3)–C(7) and C(8)–C(12) rings.

¹ Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Atomic coordinates and equivalent isotropic displacement parameters for $[(\text{C}_5\text{H}_5)_2\text{Ta}(\text{CO})(\mu, \eta^1: \eta^1\text{-PMe}_2\text{S})\text{W}(\text{CO})_5]$ (**10'a**)

Atom	x	y	z	U_{eq}^1 (\AA^2)
W	0.0962(1)	0.2348(1)	0.4563(1)	41(1)
C(1)	-0.1546(34)	0.1989(11)	0.4326(24)	70(11)
O(1)	-0.2824(23)	0.1802(9)	0.4185(19)	104(10)
C(2)	0.1172(30)	0.2150(11)	0.6061(23)	65(10)
O(2)	0.1224(23)	0.2106(10)	0.6989(16)	91(9)
C(3)	0.0646(31)	0.2638(9)	0.3108(19)	53(9)
C(3)	0.0272(21)	0.2820(7)	0.2253(13)	65(7)
C(4)	0.3669(44)	0.2623(13)	0.4698(24)	122(15)
O(4)	0.4830(22)	0.2815(10)	0.4879(17)	100(10)
C(5)	0.0276(34)	0.3167(11)	0.4887(20)	70(11)
O(5)	-0.0127(27)	0.3677(8)	0.5043(15)	91(9)
S	0.1951(8)	0.1225(3)	0.4324(4)	49(2)
P	0.1956(6)	0.0971(2)	0.2800(4)	32(2)
C(7)	0.3148(23)	0.1549(9)	0.2160(16)	47(8)
C(8)	-0.0212(24)	0.1114(9)	0.2041(16)	53(8)
Ta	0.3001(1)	-0.0135(1)	0.2597(1)	29(1)
C(6)	0.2457(27)	-0.0028(13)	0.1068(19)	67(10)
O(6)	0.2052(18)	-0.0017(9)	0.0137(12)	72(7)
CNT(1)	0.5668	-0.0104	0.2827	
CNT(2)	0.1061	-0.0678	0.3025	
C(11)	0.5742(23)	-0.0220(9)	0.3759(16)	44(7)
C(12)	0.5748(23)	-0.0659(9)	0.2920(19)	46(8)
C(13)	0.5664(25)	-0.0336(10)	0.1957(21)	53(9)
C(14)	0.5570(22)	0.0314(10)	0.2199(17)	42(7)
C(15)	0.5615(21)	0.0383(9)	0.3299(17)	42(7)
C(16)	0.2103(34)	-0.1043(13)	0.3314(21)	60(10)
C(17)	0.1602(27)	-0.0594(11)	0.3925(18)	49(8)
C(18)	0.0314(35)	-0.0252(11)	0.3257(24)	77(12)
C(19)	0.0039(31)	-0.0492(13)	0.2289(21)	68(11)
C(20)	0.1247(37)	-0.1008(12)	0.2339(29)	92(15)

CNT(1) and CNT(2) are the gravity centers of the C(11)–C(15) and C(16)–C(20) rings.

¹ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$[\text{Cp}_2\text{Nb}(\text{CO})(\mu, \eta^1: \eta^1\text{-PMe}_2\text{S})\text{Fe}(\text{CO})_4]$ (12a**):** Anal. Found: C, 39.9; H, 3.2. $\text{C}_{17}\text{H}_{16}\text{FeNbO}_5\text{PS}$ calc.: C, 39.8; H, 3.1%. IR (CsI): $\nu(\text{P}=\text{S})$ 500 cm^{-1} . IR (THF): $\nu(\text{CO})$ 2023, 1934, 1920, 1908 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 5.58 (d, $J = 2$ Hz, Cp); 1.73 (d, $J = 8$ Hz, Me). ^{31}P NMR (CD_3COCD_3): δ 30 (s).

3.2.8. $[\text{Cp}_2\text{M}(\text{CO})(\mu, \eta^1: \eta^1\text{-PPh}_2\text{O})\text{SnBu}_3\text{Cl}]$ (**13b**; **13'b**)

A 250 mg (0.57 mmol) sample of **1b** $[\text{Cp}_2\text{Nb}(\text{CO})(\text{PPh}_2)]$ was dissolved in 20 ml of THF. The solution was treated with one equivalent of Bu_3SnCl . After 5 min, the solvent removed and the pink solid was washed with pentane.

$[\text{Cp}_2\text{Nb}(\text{CO})(\mu, \eta^1: \eta^1\text{-PPh}_2\text{O})\text{SnBu}_3\text{Cl}]$ (13b**):** IR (CsI): $\nu(\text{P}=\text{O})$ 1013 cm^{-1} . IR (THF): $\nu(\text{CO})$ 1932 cm^{-1} . ^1H NMR (CD_3COCD_3): δ 7.60–7.40 (m, Ph); 5.30 (d, $J = 2$ Hz, Cp); 1.71 (m, CH_2); 1.32 (m, CH_2); 1.13 (m, CH_2); 0.83 (t, $J = 7$ Hz, CH_3). ^{31}P NMR (CD_3COCD_3): δ 121 (s).

[Cp₂Ta(CO)(μ, η¹: η¹-PPH₂O)SnBu₃Cl] (13'b): IR (CsI): ν(P=O) 1020 cm⁻¹. IR (THF): ν(CO) 1917 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 7.70–7.40 (m, Ph); 5.25 (d, J = 2 Hz, Cp); 1.70 (m, CH₂); 1.28 (m, CH₂); 1.19 (m, CH₂); 0.83 (t, J = 7 Hz, CH₃). ³¹P NMR (CD₃COCD₃): δ 95 (s).

3.3. Crystal structure analyses

Crystals of **4b** (orange; 0.25 × 0.20 × 0.20 mm) and of **10'a** (red; 0.19 × 0.38 × 0.76 mm) were mounted on Enraf–Nonius CAD4 and AED II (Siemens–Stoe) diffractometers, respectively. The crystal data and data collection parameters are summarized in Table 2. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (Ψ scan) was made for both structures. The Enraf–Nonius SDP library [24] was used for data reductions, and the solution and refinement of the structure of **4b** were performed with SHELX76 programs [25a]. All calculations concerning the structure of **10'a** were carried out with SHELXTL PLUS programs [25b]. Neutral-atom scattering factors and anomalous dispersion corrections were those given by Cromer and Waber [26]. Both structures were solved and refined by conventional three-dimensional Patterson, difference Fourier and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were placed in calculated positions riding on the carbon atoms bearing them and included in the final calculations with B_{iso} fixed at the values equal to $1.3B_{\text{eq}}$ for the corresponding carbon atoms in **4b** and for **10'a**; all H atoms were fixed at $U_{\text{eq}} = 0.08$. Final positional parameters of non-hydrogen atoms for **4b** and **10'a** are given in Tables 3 and 4 respectively.

4. Supplementary material available

Tables of the anisotropic thermal parameters, hydrogen atom coordinates, full tables of bond distances and angles, and least-squares planes for **4b** and **10'a** have been deposited at the Cambridge Crystallographic Data Centre. Listings of observed and calculated structure factors for **4b** and **10'a** are available from the authors.

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