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Reactions of (phosphine)pentacarbonyltungsten. Synthesis of primary and secondary phosphines in the coordination sphere of tungsten

François Nief, François Mercier and François Mathey *

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex (France)

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Abstract

A new preparation of $W(CO)_5(PH_3)$ (**1**) in fair yield on a multigram scale has been devised. **1** is metalated by one equivalent of n-BuLi to give $W(CO)_5(PH_2Li)$ (**2**), which reacts with various electrophiles: with alkyl halides $W(CO)_5(PH_2R)$ complexes are obtained, but with other electrophiles the species $W(CO)_5(PHR_2)$ is also obtained along with **1**. Disubstituted complexes can also be obtained when **1** is treated with an excess of n-BuLi followed by an excess of an electrophile. The results are rationalized by postulating that polysubstituted compounds are obtained by stepwise deprotonation of less-substituted complexes rather than via polylithiated complexes such as $W(CO)_5(RPLi_2)$ or $W(CO)_5(PLi_3)$. A one-pot preparation of $W(CO)_5[P(SiMe_3)_3]$ in good yield from **1** was also achieved. The intermediate $W(CO)_5[LiP(SiMe_3)_2]$ was also made from **1**, and its reaction with $BrCH_2Cl$ followed by hydrolysis gave $(CO)_5W(PH_2CH_2PH_2)W(CO)_5$.

Introduction

The chemistry of transition metal complexes of primary and secondary phosphines is much less developed than that of tertiary phosphine complexes. One of the reasons for this is that primary and secondary phosphines are much less readily available than tertiary phosphines, especially in the primary species which are highly toxic, spontaneously flammable gases or low-boiling liquids. Yet these phosphines are of interest as ligands because of their small bulk and the potential reactivity of the P–H bonds. An attractive route to transition metal complexes of these phosphines would involve the transformation of a phosphine precursor in the coordination sphere of a metal, a route which has not been much studied [1] but is of current interest to us [2]. The simplest precursor would be a complex of the parent phosphine, and indeed conversion of a manganese complex of PH_3 into a tertiary

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phosphine complex has already been achieved [3]. We thus decided to study the chemistry of $W(CO)_5(PH_3)$, with the aim of converting this compound into a series of primary or secondary phosphine complexes. However, all published syntheses [4] of this precursor involved the use of gaseous PH_3, which is as air-sensitive and toxic as the low molecular weight primary and secondary phosphines, and so we had to devise a new method for the preparation of $W(CO)_5(PH_3)$.

Results

Synthesis of W(CO)$_5$(PH$_3$)

There are several "phosphine equivalents" that generate phosphine under certain conditions, e.g. $P(CH_2OH)_3$ and PH_4I. The latter, which is commercially available, readily dissociates into PH_3 and HI, and has already been used to prepare nickel complexes of phosphine [5]. We therefore treated PH_4I with $W(CO)_5(THF)$ (generated by photolysis) or $W(CO)_5(CH_3CN)$ [6] in THF solution, and obtained, after simple work-up, a fair yield (60%) of the desired $W(CO)_5(PH_3)$ (**1**).

$$W(CO)_5(L) \xrightarrow[PH_4I]{THF} \underset{(1)}{W(CO)_5(PH_3)}$$

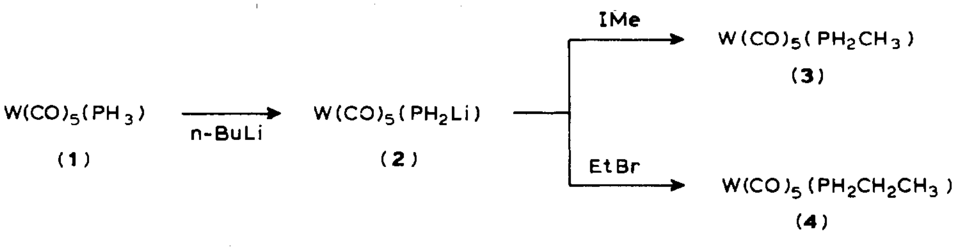
$$(L = THF, CH_3CN)$$

The procedure involving $W(CO)_5(CH_3CN)$ can be easily scaled-up, thus we were able to obtain more than 10 g of **1** in one batch. The product was a fairly air-stable, odorless white solid, with physical properties identical to those previously described for **1** [4].

Reactivity of W(CO)$_5$(PH$_2$Li)

With **1** available we considered that primary phosphine complexes should be obtainable by proton abstraction from **1** and subsequent reaction of the resulting anion with an electrophile. (Metalation of $CpMn(CO)_2(PH_3)$ has already been observed [3].) Reaction of a THF or ether solution of **1** with n-BuLi cleanly gave a light yellow solution of $W(CO)_5(PH_2Li)$ (**2**), which was identified by ^{31}P NMR spectroscopy: the signal from this anion is ca. 80 ppm upfield from that of **1**, and is a triplet, indicating that only two protons are attached to phosphorus. Complex **2** was not isolated but treated in situ with various electrophiles.

We first tried simple alkyl halides. With MeI and EtBr, the reaction proceeded as expected, and isolated $W(CO)_5(PH_2CH_3)$ (**3**) and $W(CO)_5(PH_2CH_2CH_3)$ (**4**), respectively.



However, **2** did not react with n-octyl chloride at an appreciable rate, but with activated chlorides such as allyl chloride, it gave $W(CO)_5(PH_2CH_2CH{=}CH_2)$ (**5**); however, the latter was accompanied by a secondary product, which was identified as $W(CO)_5[PH(CH_2CH{=}CH_2)_2]$.

$$\mathbf{2} \xrightarrow{ClCH_2CH=CH_2} W(CO)_5(PH_2CH_2CH{=}CH_2) + \underset{(10\%)}{W(CO)_5[PH(CH_2CH{=}CH_2)_2]}$$

The low nucleophilicity of **2** is also evident from its failure to react with benzophenone or acetone. On the other hand, it does react with benzaldehyde, to give $W(CO)_5(PH_2CHOHC_6H_5)$ (**6**) (after hydrolysis):

$$\underset{(\mathbf{2})}{W(CO)_5(PH_2Li)} \xrightarrow{PhCHO,\ H_2O} \underset{(\mathbf{6})}{W(CO)_5(PH_2CHOHC_6H_5)}$$

The reaction of **2** with polyhalides of the type $X(CH_2)_nY$ (X, Y = Cl, Br; $n = 1, 2$) gave complex mixtures of products, which were not identified. For the case in which $n = 1$, the ^{31}P NMR spectrum showed only the signal for **1**. The reaction of **2** with stronger electrophiles is also complex: when **2** was treated with 1 equivalent of Me_3SiCl, the ^{31}P NMR spectrum of the reaction mixture indicated the presence of **1**, $W(CO)_5(Me_3SiPH_2)$ (**7**) and $W(CO)_5[(Me_3Si)_2PH]$ (**8**) in a 1/2/1 ratio.

$$\mathbf{2} \xrightarrow[Et_2O]{1\text{ eq. } Me_3SiCl} \mathbf{1} + \underset{(\mathbf{7})}{W(CO)_5(PH_2SiMe_3)} + \underset{(\mathbf{8})}{W(CO)_5[PH(SiMe_3)_2]}$$

(**7** $\delta(P)$ -195, $^1J(PH)$ 310 Hz (t of m); **8** $\delta(P)$ -214, $^1J(PH)$ 292 Hz (d of m))

The reaction of **1** with pivaloyl chloride did not even yield any monosubstituted compound, but only a 1/1 mixture of **1** and $W(CO)_5[PH(CO\text{-}t\text{-}Bu)_2]$ (**9**).

$$\mathbf{2} \xrightarrow[THF]{1\text{ eq. } t\text{-}BuCOCl} \mathbf{1} + \underset{(\mathbf{9})}{W(CO)_5[PH(CO\text{-}t\text{-}Bu)_2]}$$

Complexes **1** and **9** were separated by column chromatography, and **9** was crystallized.

Attempted preparation of polylithiated species

Since $CpMn(CO)_2(PLi_3)$ had been previously made by reaction of 3 equivalents of n-BuLi with $CpMn(CO)_2(PH_3)$ [3], we tried a similar approach with $W(CO)_5(PH_3)$. With more than one equivalent of n-BuLi at $-78\,°C$, a yellow-orange solution was observed; this quickly turned brown, and gave only broad peaks in the ^{31}P NMR when the spectrum was measured at room temperature, indicating decomposition. In a low temperature NMR experiment, solutions of **1** were treated with two or three equivalents of n-BuLi at $-78\,°C$, and their spectra measured at the same temperature. The three spectra were identical, with only the signal from **2** was apparent, and it is evident that no further reaction occurs between **2** and n-BuLi at low temperature. However, solutions obtained by addition of 2 or 3 eq. of n-BuLi to 1 eq. of **1** behave as if anions $W(CO)_5(PHLi_2)$ and $W(CO)_5(PLi_3)$ were indeed present in the mixture. Thus addition of 2 eq. of n-BuLi to 1 eq. of **1** followed by two eq. of t-BuCOCl gave **9** in good yield.

$$\underset{(\mathbf{1})}{W(CO)_5(PH_3)} \xrightarrow[2t\text{-}BuCOCl]{2BuLi} \underset{(\mathbf{9})}{W(CO)_5[PH(t\text{-}BuCO)_2]}$$

Similarly $W(CO)_5[P(SiMe_3)_3]$ (**10**) can be obtained in good yield by the following sequence:

$$\underset{(\mathbf{1})}{W(CO)_5(PH_3)} \xrightarrow[3Me_3SiCl]{3BuLi} \underset{(\mathbf{10})}{W(CO)_5[P(SiMe_3)_3]}$$

When 2 eq. of Me_3SiCl were added to a solution made up from 3 eq. of n-BuLi and 1 eq. of **1**, a single signal at -325 ppm was observed, and was attributed to $W(CO)_5[LiP(SiMe_3)_2]$ (**11**).

$$\underset{(\mathbf{1})}{PH_3W(CO)_5} \xrightarrow[2Me_3SiCl]{3n\text{-}BuLi} \underset{(\mathbf{11})}{W(CO)_5[LiP(SiMe_3)_2]}$$

As expected, reaction of **11** with 1 eq. of MeI followed by hydrolysis, gave **3**, which had been previously prepared:

$$\underset{(\mathbf{11})}{W(CO)_5[LiP(SiMe_3)_2]} \xrightarrow[H_2O]{ICH_3} \underset{(\mathbf{3})}{W(CO)_5(PH_2CH_3)}$$

Similarly, reaction of **11** with $BrCH_2Cl$ gave, after hydrolysis, $W(CO)_5(PH_2CH_2PH_2)W(CO)_5$ (**12**).

$$\underset{(\mathbf{11})}{W(CO)_5[LiP(SiMe_3)_2]} \xrightarrow[H_2O]{BrCH_2Cl} \underset{(\mathbf{12})}{W(CO)_5(PH_2CH_2PH_2)W(CO)_5}$$

Discussion

Primary phosphine complexes can be readily obtained by reaction of RX with $W(CO)_5(PH_2Li)$ provided that X = Br or I and that R is a simple alkyl group. In a novel preparation, a functional primary phosphine complex has been obtained by treatment of **2** with benzaldehyde; very few α-hydroxy primary phosphines are known [7]. The reason why polysubstitution occurs when stronger electrophiles react with **2** is probably that the $W(CO)_5(RPH_2)$ complex initially formed is more acidic than **1** and so is deprotonated by the remaining **2**, to give the complex $W(CO)_5(RPHLi)$, which reacts with RX to give $W(CO)_5(R_2PH)$. This problem is evident with allyl chloride, and is worst with pivaloyl chloride, from which no monosubstituted product is obtained. An alternative possibility is that **2** disproportionates into **1** and $W(CO)_5(PLi_2H)$, but this seems unlikely since no complex other than **2** was detectable by ^{31}P NMR spectroscopy in solutions of **2** in the presence of excess n-BuLi. However, such solutions, behave as if $W(CO)_5(PLi_2H)$ or $W(CO)_5(PLi_3)$ were indeed present in terms of their reactions with electrophiles RX. This apparent paradox can be explained by assuming that in this case n-BuLi acts simply as a base, and that its nucleophilic reaction with the CO ligands in the $LW(CO)_5$ complexes or with RX is much slower than proton abstraction from the $W(CO)_5(R_nPH_{3-n})$ species, and so n-BuLi deprotonates the latter species as soon as they are formed in the reaction mixture. When 3 eq. of n-BuLi and 3 eq. of electrophile are used, either the only product is the trisubstituted phosphine complex ($R = SiMe_3$), or the reaction stops at the $W(CO)_5(R_2Li)$ stage when this species is unreactive towards RX (R = CO-t-Bu); in the latter case $W(CO)_5(R_2PH)$ is obtained after hydrolysis. A $W(CO)_5(R_2PLi)$ complex can also be obtained by addition of 2 eq. of RX to a solution containing 1 eq. of **2** and 2 eq. of n-BuLi. This complex ($W(CO)_5[LiP(SiMe_3)_2]$ (**11**)) can be regarded as a synthetic equivalent of $W(CO)_5(PH_2Li)$ (**2**) and a complex, **12**, of the bidentate phosphine $PH_2CH_2PH_2$ has been obtained by treating **11** with $BrCH_2Cl$ followed by hydrolysis, a procedure that failed when the starting material was **2**. We are now currently investigating the synthetic usefulness of complex **11**.

Experimental

General

All reactions were performed under argon. NMR spectra were recorded on a multinuclear WP80 SY spectrometer operating at 80.13 (^1H), 20.15 (^{13}C) and 32.44 (^{31}P) MHz; chemical shifts are in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in Hz.

Mass spectra were recorded on a Shimadzu GC-MS 1000 instrument at 70 eV. Infrared spectra were obtained with a Perkin–Elmer model 297 spectrometer. Elemental analyses were performed by the Service Central d'Analyses du CNRS. Silica gel was used for chromatographic separations.

Syntheses

(Phosphine)pentacarbonyltungsten (1)

Method A. A solution of $W(CO)_5THF$ was prepared by irradiation for 1 h of a solution of $W(CO)_6$ (3.5 g, 10 m*M*) in 250 ml THF with a 125 W medium-pressure mercury vapor lamp, and solid PH_4I (1.62 g, 10 m*M*) was then added. After 1 h stirring, the mixture was evaporated to dryness and the residue dissolved in a small amount of toluene. The solution was filtered through a short column of silica gel and evaporated to dryness to yield 2.2 g (6.1 m*M*, 61%) of crude product, which was recrystallized from ethanol.

Method B. To a stirred suspension of 17.4 g (50 m*M*) of $W(CO)_6$ in 250 ml CH_3CN, was added 5.56 g (50 m*M*) of $Me_3NO \cdot 2H_2O$, in small portions, during 1/2 h. The yellow solution was stirred for a further 30 min, then evaporated to dryness in vacuo. The residue was dissolved in dry toluene and the solution evaporated to dryness. The crude $W(CO)_5(CH_3CN)$ thus obtained was dissolved in 250 ml of dry THF, and the solution was transferred to a 500 ml single-necked screw-capped vessel and 10 g (61.7 m*M*) of PH_4I was added. The vessel was stoppered, the mixture was stirred for 24 h, and the vessel then opened. The solution was evaporated to dryness and work up was as in Method A. The yield of recrystallized product was 11 g (30.7 m*M*, 61%). M.p. 136°C (Lit. 4 120°C). ^{31}P NMR −183 ppm ($^1J(PH)$ 337, $^1J(PW)$ 216 Hz).

(Lithium phosphide)pentacarbonyltungsten (2)

To a solution of 500 mg 1.4 m*M*) of **1** in 10 ml of THF at −78°C was added 0.87 ml of 1.6 *M* n-BuLi in hexane (1.4 m*M*). The light yellow solution of **2** obtained displayed a single ^{31}P NMR peak at −273 ppm (triplet, $^1J(PH)$ 156, $^1J(PW)$ 68 Hz). This solution was used for the following syntheses.

(Methylphosphine)pentacarbonyltungsten (3)

To a solution of **2**, prepared as described above, 0.1 ml (227 mg, 1.6 m*M*) of CH_3I was added at room temperature. The mixture was stirred for 5 min, then evaporated to dryness and chromatographed (pentane/toluene 80/20). The colorless, air-sensitive malodorous solid obtained (375 mg, 1.01 m*M*, 70%), was purified by short-path distillation at 70 °C/0.1 mmHg. M.p. 33 °C. ^{31}P: -123.7 (^1J(PW) 225 Hz) ($CDCl_3$); ^1H: 1.71 (q, ^3J(HH) $\simeq$ ^2J(PH) = 7.0 Hz, CH_3), 4.63 (dq, ^1J(PH) 335.5, ^2J(PH) 7.0, PH_2); ^{13}C: 4.70 (d, ^1J(PC) 31.8 Hz, CH_3), 195.5 (d, ^2J(PC) 7 Hz *cis* CO), 198.4 (d, ^2J(PC) 22 Hz, *trans*-CO); IR ν(C=O) 2077, 1943 cm^{-1}. Anal. Found: C, 19.38; H, 1.36. $C_6H_5O_5PW$ calc. C, 19.38; H, 1.36%.

(Ethylphosphine)pentacarbonyltungsten (4)

The procedure was as described for **3**, but 0.12 ml of ethyl bromide (1.6 m*M*) was used. A colorless, air sensitive malodorous liquid was obtained (420 mg, 1.09 m*M*, 78%) and was purified by short-path distillation at 100 °C/0.1 mmHg ^{31}P: -95.5 (^1J(PW) 216.5 Hz) (C_6D_6); ^1H: 0.74 (m, CH_3), 1.15 (m, CH_2), 3.68 (dt, ^1J(PH) 334, ^2J(PH) 6.4 Hz, PH_2) (C_6D_6); ^{13}C: 15.4 (^2J(PC) 6.5 Hz, CH_2), 15.9 (^1J(PC) 30.2 Hz, CH_3), 196.6 (d, *J*(PC) 7, *cis* CO) (C_6D_6); *trans* CO was not detected. Mass spec. *m/e* 386 (M^+, 100%). Anal. Found: C, 22.13; H, 1.97. $C_7H_7O_5PW$ calc: C, 21.78; H, 1.83%.

(2-Propen-1-yl phosphine)pentacarbonyltungsten (5)

The procedure was as described for **3** but 0.13 ml of allyl chloride (1.6 m*M*) was used. The light yellow, air sensitive malodorous liquid obtained (400 mg, 1 m*M*, 71%) was purified by short-path distillation at 130 °C/0.1 mmHg. ^{31}P: -99.6 (^1J(PW) 220 Hz) (C_6D_6); ^1H: 2.00 (m, PH_2CH_2-), 3.75 (dt, ^1J(PH) 335, ^2J(PH) 6.5 Hz, PH_2), 5.2 (m, $CH{=}CH_2$) (C_6D_6); ^{13}C: 26.8 (d, ^1J(PC) 28.4 Hz, P-CH_2), 119.3 (d, ^3J(PC) 10.7 Hz, $=CH_2$), 134.1 (d, ^2J(PC) 9.5 Hz, -CH=), 196.5 (d, ^2J(PC) 7 Hz, *cis* CO) (C_6D_6); *trans* CO was not detected. Mass spec. *m/e* 398 (M^+, 100%). IR ν(C=O) 2085, 1940 cm^{-1}. Anal. Found: C, 23.61; H, 1.74. $C_8H_7O_5PW$ calc: C, 24.14; H, 1.77%.

(α-Hydroxybenzyl phosphine)pentacarbonyltungsten (6)

To a solution of **2** at room temperature was added 0.2 ml (1.96 m*M*) of benzaldehyde. The mixture was stirred for 5 min then treated with dilute HCl. The THF solution was dried and evaporated to dryness, and the residue chromatographed (in dichloromethane). The solid obtained, was rinsed with n-pentane and dried. Yield 300 mg (0.65 m*M*, 46%). m.p. 76 °C. ^{31}P: -59.6 (^1J(PW) 220 Hz) ($CDCl_3$); ^1H: 4.09 (dd, ^1J(PH) 333.5, ^3J(HH) 3.9 Hz, PH_2), 4.44 (q, ^2J(PH) = ^3J(HH) = 3.9 Hz, CHOH), 7.0 (m, 5H, Ph) ($CDCl_3$); ^{13}C: 71.4 (d, *J* 36.5, -CHOH-), 125.9, 125.6 (s, C *ortho* and C *para*), 129.2 (s, C *meta*), 140.1 (s, C_α), 194.9 (d, *J* 6 Hz, *cis* CO) ($CDCl_3$); *trans* CO was not detected. Mass spec.: *m/e* 464 (M^+, 30%), 380 ($M-3CO$, 25%), 358 ($M-$PhCHO, 100%). IR ν(CO) 2077, 1950 cm^{-1}. Anal. Found: C, 30.67; H, 2.01. $C_{12}H_9O_6PW$ calc: C, 31.00; H, 1.9%.

[Bis(2,2-dimethyl propionyl)phosphine]pentacarbonyltungsten (8)

To a solution of 500 mg of **7** in 10 ml of THF, at −78 °C, was added 1.75 ml of 1.6 *M* n-BuLi in hexane (2.8 m*M*), followed by 0.35 ml (2.84 m*M*) of pivaloyl chloride. The solution was allowed to warm to room temperature then evaporated to dryness, and the residue chromatographed (in toluene). 440 mg (60%) of **8** were obtained and recrystallized from hexane/toluene, m.p. 129 ° C. ^{31}P: -59.69 (^1J(PW) 212 Hz) ($CDCl_3$); ^{1}H: 1.29 (s, C(CH_3)$_3$), 7.06 (d, ^1J(PH) 324 Hz, P*H*) ($CDCl_3$); ^{13}C: 26.0 (s, C(*C*H_3)$_3$), 49.8 (d, ^2J(PC) 31.7 Hz, *C*(CH_3)$_3$), 195.2 (d, ^2J(PC) 5 Hz, *cis* CO), 197.2 (d, ^2J(PC) 25.5 Hz, *trans* CO), 213.5 (d, ^1J(PC) 9.8 Hz, *C*O-t-Bu) ($CDCl_3$). Mass spec. *m/e* 526 (M^+, 20%), 498 ($M-$ CO, 100%). IR ν(C=O) 2075, 1950 cm^{-1}. Anal. Found: C, 34.41; H, 3.63; P, 5.74. $C_{11}H_{19}O_5PSi_2W$ calc: C, 34.25; H, 3.64; P, 5.85%.

[Tris(trimethylsilyl)phosphine]pentacarbonyltungsten (10)

To a solution of 720 mg (2 m*M*) of $W(CO)_5PH_3$ in 20 ml of ether at −78 ° C, was added 3.75 ml of 1.6 *M* n-butyllithium (6 m*M*) and then 0.75 ml (660 mg, 6 m*M*) of Me_3SiCl. The mixture was allowed to warm to room temperature and then evaporated to dryness. The residue was taken up in toluene, and the solution filtered then evaporated to dryness to leave crystals of **10** (850 mg, 1.48 m*M* and 74%). M.p. 170 ° C. ^{31}P: −252 (^1J(PW) 147 Hz) (Lit. 8 −251.5, ^1J(PW) 150.9 Hz); ^{1}H: 0.22 (d, ^3J(PH) 5.1 Hz). Mass spec.: *m/e* 574 (M^+, 46%), 518 ($M-$ 2CO, 100%).

[$\mu:\eta^1,\eta^1$(Diphosphinomethane)]octacarbonylditungsten (12)

To a solution of 700 mg (2 m*M*) of **1** in 10 ml of THF at −78 ° C was added 4 ml of 1.5 *M* n-BuLi in hexane (6 m*M*) and then 0.3 ml of Me_3SiCl (4 m*M*). To the solution of **11** thus formed, still at −78 ° C, was added 0.25 ml (4 m*M*) of $BrCH_2Cl$. The solution was then allowed to warm to 0 ° C, and then treated with 2*N* HCl. The organic layer was evaporated to dryness, the residue taken up in ether, and the solution dried, evaporated to dryness, then chromatographed on short silica gel column (hexane/toluene 1/1). The eluate was evaporated to dryness and the residue recrystallized from hexane/toluene 1/1. Yield 440 mg (0.6 m*M*, 60%). m.p. 160 ° C. ^{31}P: −93.2 (J(PW) 240 Hz) (CD_3COCD_3); ^{1}H{^{31}P}: 2.41 (quintet, ^3J(HH) 6.7 Hz, CH_2P), 5.07 (t, ^3J(HH) 6.7 Hz, PH_2); ^{1}H: 2.41 (m), 5.05 (dm, ^1J(PH) $\approx$ 340 Hz) (CD_3COCD_3); ^{13}C: 11.65 (t, ^1J(PC) 18.31 Hz, *C*H_2), 196.16 (ps t, J 7.20 Hz, CO) (CD_3COCD_3); *trans* CO was not detected. IR (decalin) ν(C=O) 2070, 1953 cm^{-1}. Mass spec.: *m/e* 728 (M^+, 100%). Anal. Found: C, 19.32; H, 1.05; P, 8.76; W, 50.90. $C_{12}H_8O_{10}P_2W_2$ calc: C, 18.09; H, 0.81; P, 8.51; W, 50.50%.

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