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Syntheses and Structures of Tungsten *o*-(Diphenylphosphino)benzaldehyde Complexes Bearing *π*-Bonded Aldehyde Groups

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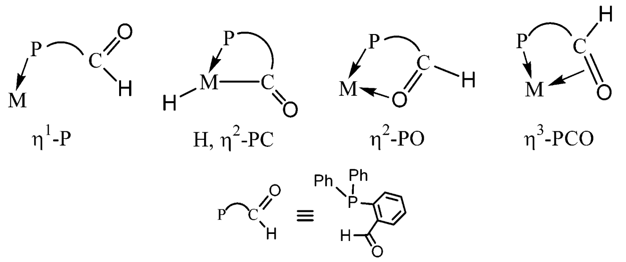
Summary: Reaction of the bidentate ligand $Ph_2P(o\text{-}C_6H_4)C(=O)H$ *(abbreviated as PCHO) with* $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ *at room temperature affords* $W(CO)_3(\eta^1\text{-}PCHO)(\eta^3\text{-}PCHO)$ *(**1**), which subsequently loses a carbonyl ligand to give* $W(CO)_2(\eta^3\text{-}PCHO)_2$ *(**2**). Further treatment of **2** with PCHO in refluxing benzene results in carbon−carbon coupling of the PCHO ligands to produce* $W(CO)(\eta^3\text{-}PCHO)(\eta^3\text{-}(PCHO)_2)$ *(**3**). The structures of **1**−**3** have been determined by an X-ray diffraction study. The PCHO ligands in these compounds act as chelating phosphine−aldehydes with the aldehyde groups coordinating in a π fashion.*

Introduction

Chelating ligands containing "soft" phosphorus and "hard" nitrogen or oxygen donor atoms can alter the reactivity of metal centers and may be of interest in the design and development of new homogeneous catalytic systems.[1] The *o*-(diphenylphosphino)benzaldehyde molecule ($Ph_2P(o\text{-}C_6H_4)C(=O)H$; abbreviated as PCHO) is one of the simplest bidentate P,O-chelating agents.[2] Four binding modes, depicted in Chart 1, have been observed for PCHO in its reactions with transition-metal complexes. Usually, the phosphine center is coordinated to a metal in advance of the aldehyde group and can serve as a monodentate η^1-P donor in $W(CO)_5(PCHO)$,[3] $RhCl(CO)(PCHO)_2$,[4] and $(Rh(CO)(PCHO)(\mu\text{-}pz))_2$ (pz = pyrazolate).[5] Subsequent oxidative addition of the aldehyde C−H bond on a Rh(I),[6] Ir(I),[7] Pt(0),[8] or Co(I)[9] center can generate a phosphine−acyl hydrido complex (H,η^2-PC mode). On the other hand, the PCHO ligand can act as a chelating phosphine−aldehyde with the aldehyde moiety bonded to a metal in a σ fashion through the oxygen atom (η^2-PO mode), or in a π fashion through the carbon−oxygen double bond (η^3-PCO mode). The η^2-PO bonding feature was found in $Re(CO)_3Cl(PCHO)$[10] and $RuCl_3(PCHO)_2$,[7a] while the η^3-PCO bonding feature has only been suggested for Cp*Co(PCHO)[11] on the basis of NMR spectral data. In this paper we wish to report three structurally characterized tungsten PCHO complexes containing π-bonded aldehyde groups.

Chart 1



Results and Discussion

Previously, reactions of the triazacyclohexane complex $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ with diphenylacetylene and bis(diphenylphosphino)acetylene have been reported to give the tris(alkyne) complex $W(CO)(PhC{\equiv}CPh)_3$[12] and the ditungsten helical complex $W_2(CO)_6(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_3$,[13] respectively. On the other hand, treatment of $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ with 3 equiv of PCHO ligand at room temperature affords the bis-PCHO complex $W(CO)_3(\eta^1\text{-}PCHO)(\eta^3\text{-}PCHO)$ (**1**) in 54% yield after crystallization from *n*-hexane/dichloromethane. During

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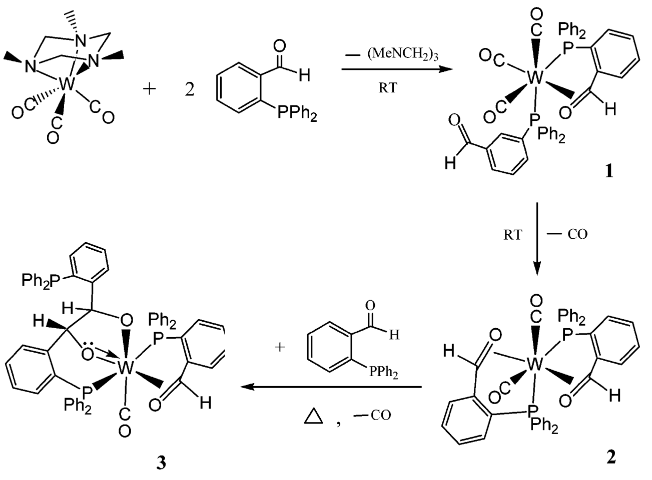
Scheme 1



the reaction, the solution color changed from brown to purple, and IR analysis showed complete substitution of the coordinated triazacyclohexane ligand after 30 min, at which point the reaction mixture was worked up. Although compound **1** is stable as a solid, in solution it undergoes a facile decarbonylation reaction to generate $W(CO)_2(\eta^3\text{-PCHO})_2$ (**2**). Alternatively, compound **2** can be synthesized directly from the reaction of $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ and PCHO in dichloromethane at room temperature over a period of 48 h. There is no further reaction between **2** and PCHO at room temperature, but this mixture leads to the dioxyl complex $W(CO)(\eta^3\text{-PCHO})(\eta^3\text{-}(PCHO)_2)$ (**3**; 44% yield) in refluxing benzene for 21 h. The results are summarized in Scheme 1.

Compound **1** forms a purple crystalline solid. The IR spectrum in the CO region presents three absorption peaks with the pattern consistent with a *fac*-$W(CO)_3$ configuration.[14] The $^{31}P\{^1H\}$ NMR displays two doublets at δ 12.16 and 21.50 (J_{P-P} = 20 Hz), with both accompanied by ^{183}W satellites (J_{P-W} = 108 Hz), for the coordinated phosphorus atoms. The ^1H NMR spectrum shows an aldehyde proton resonance at δ 9.79, which compares with δ 10.50 for the free PCHO ligand, and an aldehyde proton resonance shifted upfield to δ 6.28, indicating coordination of one aldehyde group. The $^{13}C\{^1H\}$ NMR spectrum shows the coordinated and the pendant aldehyde carbon resonances at δ 99.4 and 190.6, respectively.

The molecular structure of **1**, shown in Figure 1, appears as a distorted octahedron. Three carbonyl ligands are terminally bonded to the W atom in a facial configuration, with the C−W−C angles in the range 82.5(2)−89.8(2)°. One PCHO ligand is chelated to the W atom with the aldehyde group in a π-donation feature, while the other PCHO ligand is η^1-bonded to the W atom through the phosphorus atom. The two W−P lengths are about equal, being 2.568 ± 0.006 Å. The pendant aldehyde group (C23−O5 bond) is coplanar with the connecting arene ring, while the coordinated aldehyde group (C4−O4 bond) is bent away from the adjacent arene plane with the torsional angle O4−C4−C5−C10 = 44.41°. The C4−O4 length (1.319(6) Å) is ca. 0.1 Å longer than that in the pendant aldehyde group (C23−O5 = 1.217(6) Å), suggesting a significant π-back-donation from the tungsten to the π^* orbital of the C═O double bond.

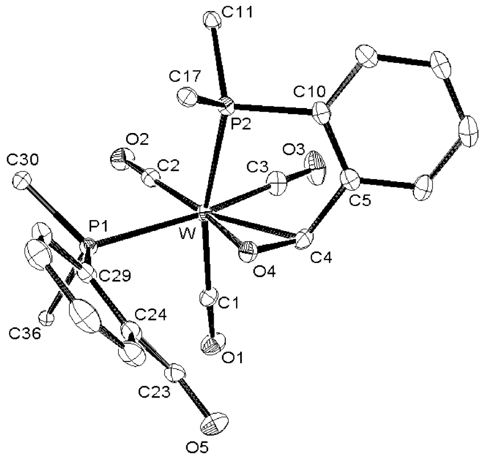


Figure 1. Molecular structure of **1**. The C_6H_5 groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond distances (Å): W−P1 = 2.563(1), W−P2 = 2.573(1), W−C1 = 1.966(5), W−C2 = 2.002(5), W−C3 = 1.993(5), W−C4 = 2.289(5), W−O4 = 2.155(3), C4−O4 = 1.319(6), C23−O5 = 1.217(6). Selected bond angles (deg): P1−W−C3 = 166.8(2), P2−W−C1 = 165.8(1), C2−W−C4 = 157.3(2), C2−W−O4 = 167.6(2), C10−P2−W = 101.1(2), C29−P1−W = 114.5(2), C5−C4−O4 = 119.2(4), C24−C23−O5 = 123.7(5).

Compound **2** forms air-stable, bright yellow crystals. The IR spectrum displays two CO absorptions at 1974 and 1910 cm^{-1}. The FAB mass spectrum gives the molecular ion at *m*/*z* 820, corresponding to a $W(CO)_2$ segment plus two PCHO ligands. However, the $^{31}P\{^1H\}$ NMR shows only one resonance at δ 10.03 accompanied by ^{183}W satellites (J_{P-W} = 112 Hz), the ^1H NMR shows a singlet at δ 5.12 for the coordinated aldehyde protons, and the $^{13}C\{^1H\}$ NMR shows the aldehyde carbon resonance at δ 81.4. These NMR data suggest the same coordination mode for the two PCHO ligands.

The molecular structure of **2** is illustrated in Figure 2. There are two terminal carbonyl ligands in cis positions with a C1−W−C2 angle of 86.7(2)°. The two PCHO ligands are coordinated to the W atom in an η^3 fashion. The two phosphorus atoms are cis to each other with W−P1 and W−P2 lengths of 2.586(1) and 2.559(1) Å, respectively, and a P1−W−P2 angle of 100.1(1)°. The two aldehyde groups are in trans positions and are η^2-bonded to the W atom with the distances C3−W = 2.218(4) Å, O3−W = 2.065(3) Å, C22−W = 2.206(4) Å, and O4−W = 2.066(3) Å. The C3−O3 and C22−O4 vectors, which are bent away from the adjacent arene planes by 54.0° (average), are about perpendicular to each other, presumably to obtain better π-back-donation from separate filled d orbitals of the tungsten metal.

The FAB mass spectrum of **3** gives the molecular ion at *m*/*z* 1083, which is equal to combination of a W(CO) moiety and three PCHO molecules. The IR spectrum shows only one CO stretching absorption at 1897 cm^{-1}. In contrast to **1** and **2**, the $^{31}P\{^1H\}$ NMR spectrum of **3** is more complicated, displaying two doublets at δ 22.42 and 14.56 (J_{P-P} = 286 Hz), with both being accompanied by ^{183}W satellites (J_{P-W} = 169 and 149 Hz), and a singlet at δ −20.02 for a pendant phosphine group. The large $^{31}P-^{31}P$ coupling constant suggests a trans arrangement

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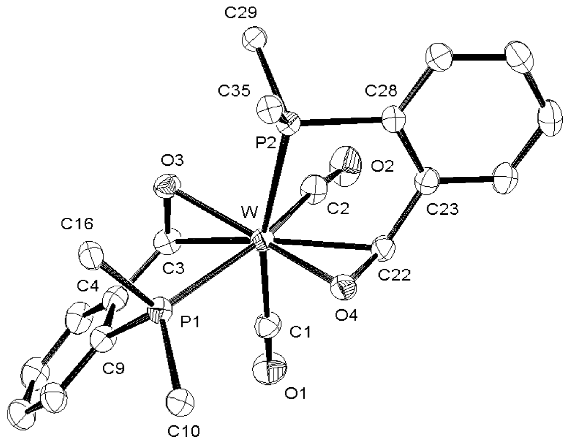


Figure 2. Molecular structure of **2**. The C_6H_5 groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond distances (Å): W−P1 = 2.586(1), W−P2 = 2.559(1), W−C1 = 1.994(5), W−C2 = 1.994(5), W−C3 = 2.218(4), W−O3 = 2.065(3), W−C22 = 2.206(4), W−O4 = 2.066(3), C3−O3 = 1.338(5), C22−O4 = 1.357(5). Selected bond angles (deg): P1−W−C2 = 165.0(1), P2−W−C1 = 166.7(1), C3−W−C22 = 152.7(2), C3−W−O4 = 155.2(1), O3−W−O4 = 155.0(1), O3−W−C22 = 154.7(1), C9−P1−W = 99.6(2), C28−P2−W = 101.8(1), C23−C22−O4 = 117.3(4), C4−C3−O3 = 120.1(4).

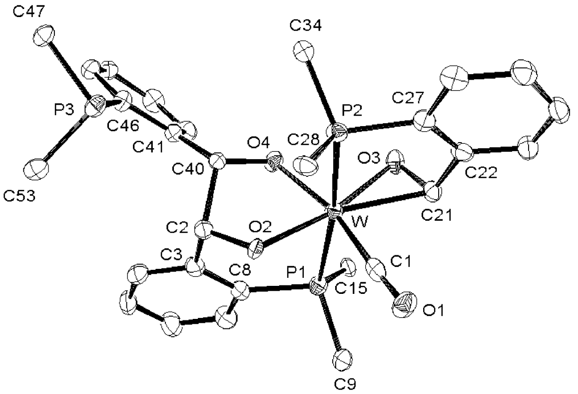
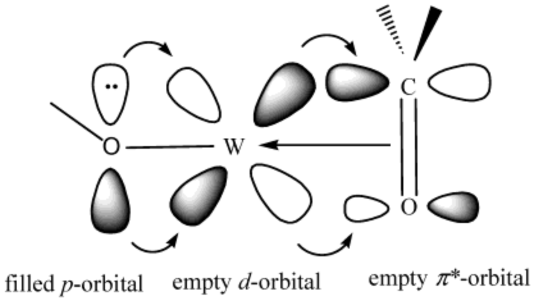


Figure 3. Molecular structure of **3**. The C_6H_5 groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond distances (Å): W−P1 = 2.522(3), W−P2 = 2.503(3), W−C1 = 1.95(1), W−C21 = 2.18(1), W−O3 = 1.948(7), W−O2 = 1.945(6), W−O4 = 2.091(7), C1−O1 = 1.17(1), C21−O3 = 1.36(1), C2−O2 = 1.42(1), C40−O4 = 1.39(1), C2−C40 = 1.57(1). Selected bond angles (deg): P1−W−P2 = 173.02(9), O4−W−C1 = 166.7(3), O2−W−C21 = 157.3(3), O2−W−O3 = 164.6(3), C22−C21−O3 = 116.8(9), C3−C2−O2 = 113.3(8), C3−C2−C40 = 112.7(8), O2−C2−C40 = 103.5(8), C2−C40−O4 = 105.8(8), C41−C40−C2 = 115.5(8), O4−C40−C2 = 105.8(8).

for the two coordinated phosphines. Furthermore, in addition to the phenyl proton resonances, the ^1H NMR spectrum shows two 1H multiplets at δ 6.44 and 6.05 and one 1H singlet at δ 6.00. Because of the absence of diagnostic spectral features to reveal the structure of **3**, a single-crystal X-ray diffraction study was performed.

The molecular structure of **3** is depicted in Figure 3, in which the tungsten atom is bonded to terminal CO, η^3-PCHO, and η^3-$Ph_2P(o\text{-}C_6H_4)CH(O-)CH(O-)(o\text{-}C_6H_4)PPh_2$ ligands. The atoms C21, O3, W, C1, O1, O2, and O4 are about coplanar, while the two phosphorus atoms are on opposite sides with a P1−W−P2 angle of 173.02(9)°. The aldehyde C21−O3 bond is bent away from the adjacent arene plane by 61.6°. The dioxyl group is apparently derived from coupling of two aldehyde carbons of the PCHO ligands.[15] The bond angles surrounding the C2 and C40 atoms are in the range 103.5(8)−115.5(8)° (average 110.2°), consistent with an sp^3 hybridization. The C40−O4 and C2−O2 bonds are staggered with a torsional angle of 52.94°. Noticeably, the W−O2 bond length (1.945(6) Å) is 0.15 Å shorter than the W−O4 bond length (2.091(7) Å), and the η^2-aldehyde group is coordinated to the tungsten atom much more strongly than those in **1** and **2**, with W−C21 = 2.18(1) Å and W−O3 = 1.948(7) Å.

Chart 2



Since the carbonyl, phosphine, and η^2-aldehyde ligands are normally considered as two-electron donors, the remaining dioxyl ligand must provide six electrons to the W(II) atom to satisfy the 18-electron rule. Thus, the shorter W−O2 length in comparison with the W−O4 length can be explained by π donation of a lone pair from the O2 atom to the tungsten, giving the W−O2 bond a partial double-bond character. This π donation can be stabilized by electron delocalization over the π^* orbital of the η^2-aldehyde group (Chart 2).

The aldehyde−transition-metal complexes are well documented, where aldehydes coordinate in a σ or π fashion depending on the metals, the oxidation states, and the steric requirements of the substrate and the ancillary ligands.[16] For instance, *p*-anisaldehyde appears as a σ donor in complexation with $[TpMo(CO)(C_2Me_2)]^+$ but as a π donor with $[TpW(CO)(C_2Me_2)]^+$ (Tp = hydridotripyrazolylborate),[17] whereas the phthalaldehyde complex of [Cp*Co] contains both σ- and π-bonded aldehyde groups.[11] It has been argued that the higher electron density at the metal center favors binding of the aldehyde in a π fashion with significant backbonding from metal to the π^* orbital of the carbonyl group.[11] For compounds **1**−**3**, the phosphine ligands are good electron donors and the tungsten centers are in low oxidation states; thus, it is easy to rationalize that the aldehyde groups prefer to bind through π interactions.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk

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techniques. $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ was prepared by literature methods.[12] $Ph_2P(o\text{-}C_6H_4)C(=O)H$ (abbreviated as PCHO) was purchased from Aldrich and used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Preparation of 1. $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ (42 mg, 0.1 mmol) and dichloromethane (10 mL) were placed in an oven-dried 50 mL Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. PCHO (93 mg, 0.32 mmol) in dichloromethane solvent (5 mL) was then introduced into the flask, and the mixture was stirred at room temperature for 30 min, yielding a purple solution. The solution was filtrated under dinitrogen, and the volatile materials were removed under vacuum. The residue was crystallized from dichloromethane/*n*-hexane to afford an air-stable, purple crystalline solid of $W(CO)_3(\eta^1\text{-PCHO})(\eta^3\text{-PCHO})$ (**1**; 46 mg, 0.054 mmol, 54%). Anal. Calcd for $C_{41}H_{30}O_5P_2W$: C, 58.05; H, 3.56. Found: C, 58.40; H, 3.85. IR (CH_2Cl_2, ν_{CO}): 1972 (s), 1904 (s), 1864 (s) cm^{-1}. MS (FAB): m/z 848 (M^+, ^{184}W), $848 - 28n$ ($n = 1-3$). ^1H NMR (CD_2Cl_2, 22 °C): δ 9.79 (s, 1H, free CHO), 7.59−6.20 (m, 28H, Ph), 6.28 (s, 1H, η^2-CHO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 12.16 (d, $J_{P-P} = 20$ Hz; with ^{183}W satellites $J_{P-W} = 108$ Hz), 21.50 (d, $J_{P-P} = 20$ Hz; with ^{183}W satellites $J_{P-W} = 108$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 227.5 (m, CO), 211.6 (dd, CO, $J_{P-C} = 6$, 16 Hz), 207.6 (dd, CO, $J_{P-C} = 5$, 50 Hz), 190.6 (d, free CHO, $J_{P-C} = 8$ Hz), 153.4−127.9 (Ph), 99.4 (η^2-CHO).

Preparation of 2. A solution of PCHO (90 mg, 0.31 mmol) in dichloromethane (5 mL) was added into a flask containing $W(CO)_3(\eta^3\text{-}(MeNCH_2)_3)$ (40 mg, 0.10 mmol) and dichloromethane (10 mL). The mixture was stirred at room temperature for 48 h, showing the solution color change from brown to purple to orange. The solution was filtered under dinitrogen, and the volatile materials were removed under vacuum. The residue was crystallized from dichloromethane/*n*-hexane to afford air-stable, bright yellow crystals of $W(CO)_2(\eta^3\text{-PCHO})_2$ (**2**; 38 mg, 0.046 mmol, 46%). Anal. Calcd for $C_{40}H_{30}O_4P_2W$: C, 58.56; H, 3.69. Found: C, 58.17; H, 3.79. IR (CH_2Cl_2, ν_{CO}): 1974 (s), 1910 (s) cm^{-1}. MS (FAB): m/z 820 (M^+, ^{184}W), $820-28n$ ($n = 1-2$). ^1H NMR (CD_2Cl_2, 22 °C): δ 7.64−6.93 (m, 28H, Ph), 5.12 (s, 2H, η^2-CHO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 10.03 (s; with ^{183}W satellites $J_{P-W} = 112$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 207.1 (dd, CO, $J_{P-C} = 13$, 58 Hz), 156.3−127.8 (Ph), 81.4 (η^2-CHO).

Transformation of 1 to 2. A solution of **1** (20 mg) in dichloromethane (10 mL) was stirred at room temperature under dinitrogen. The reaction was monitored by IR to show complete conversion of **1** to **2** over a period of 48 h.

Preparation of 3. Compound **2** (22 mg, 0.027 mmol), PCHO (17 mg, 0.058 mmol), and benzene (10 mL) were added into a flask equipped with a reflux condenser. The solution was heated to reflux for 21 h under dinitrogen. The solution was cooled to room temperature, and the solvent was removed under vacuum. The residue was crystallized from dichloromethane/*n*-hexane/diethyl ether to afford air-stable, brownish yellow crystals of $W(CO)(\eta^3\text{-PCHO})(\eta^3\text{-}(PCHO)_2)$ (**3**; 13 mg, 0.012 mmol, 44%). IR (CH_2Cl_2, ν_{CO}): 1897 (s) cm^{-1}. MS (FAB): m/z 1082 (M^+, ^{184}W), 1056 ($M^+ - CO$). ^1H NMR (CD_2Cl_2, 22 °C): δ 7.57−6.48 (m, 42H, Ph), 6.44 (m, 1H, CH−O), 6.05 (m, 1H, CH−O), 6.00 (s, 1H, η^2-CHO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 22.42 (d, $J_{P-P} = 286$ Hz; with ^{183}W satellites $J_{P-W} = 169$ Hz), 14.56 (d, $J_{P-P} = 286$ Hz; with ^{183}W satellites $J_{P-W} = 149$ Hz), −20.02 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 223.0 (CO), 157.2−126.0 (Ph), 98.1 (η^2-CHO), 85.6 (d, $J_{P-C} = 30$ Hz, CH−O), 84.8 (d, $J_{P-C} = 5$ Hz, CH−O).

Table 1. Crystallographic Data for 1−3

	1	2	3
chem formula	$C_{41}H_{30}O_5P_2W$	$C_{40}H_{30}O_4P_2W$	$C_{58}H_{45}O_4P_3W$
cryst solvent			$CH_2Cl_2 + 0.5\ Et_2O$
cryst syst	monoclinic	monoclinic	triclinic
fw	848.44	820.43	1200.65
T, K	150	295	150
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	10.8844(1)	9.4288(4)	9.8218(9)
b, Å	17.7818(2)	16.9288(7)	13.754(1)
c, Å	17.5881(2)	21.2946(9)	21.2001(2)
α, deg	90	90	73.649(2)
β, deg	91.9127(3)	101.595(1)	83.467(2)
γ, deg	90	90	73.488(2)
V, Å^3	3402.18(6)	3329.6(2)	2633.0(4)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.656	1.637	1.514
μ, mm^{-1}	3.536	3.607	2.436
R1/wR2[a]	0.0356/0.0755	0.0365/0.0809	0.0690/0.1538
GOF on F^2	1.106	1.090	1.041

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum w|F_o|^4\}^{1/2}$.

Structure Determinations for 1−3. The crystals of **1**−**3** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on Nonius KappaCCD (for **2**) and Bruker Smart ApexCCD (for **1** and **3**) diffractometers, with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The θ range for data collection is 1.63−27.50° for **1**, 1.55−27.50° for **2**, and 1.00−25.00° for **3**. Of the 24 819, 33 047, and 24 760 reflections collected for **1**−**3**, 7816, 7644, and 9291 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by direct methods and refined by least-squares cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package.[18] The data collection and refinement parameters are presented in Table 1.

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Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond angles, and bond distances of **1**−**3**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Sheldrick, G. M. SHELXTL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.