CH_2Cl_2. All of the $M_2(CO)_6(eHTP)$ complexes, for example, are thermally very stable in CH_2Cl_2.

The fact that Mo(II) and W(II) oxidation states and 7-coordinate diamagnetic systems are quite common and rather stable strongly supports the proposed formulation for the tungsten photoproduct. Drew, in his extensive review on 7-coordinate metal complexes,[20a] stated that although structures for $MX_2(CO)_2$(triphos) compounds (where triphos represents a tridentate, bischelating phosphine ligand) were not known, their geometries were most likely capped octahedral in nature.

The IR spectrum of $W_2Cl_4(CO)_4(eHTP)$ is consistent with the structure shown above. Four ν_{CO} bands are observed, with three of the bands (1920, 1830, and 1810 cm^{-1}) having approximately equal intensities, while the highest energy peak (1955 cm^{-1}) is about 40% as intense as the other carbonyl bands. The two equally intense ν_{CO} peaks (1920 and 1810 cm^{-1}) would correspond to the carbonyl ligands that are trans to the external phosphine ligands and should have an idealized OC–M–CO angle of around 100–112°, while the carbonyl ligands on the other tungsten center should have a larger OC–M–CO angle of ca. 125°, which should give an intensity ratio of the two resulting carbonyl bands of ca. 33%, and this is in good qualitative agreement with the observed values.[21] It is interesting to note that the insoluble yellow solid that is occasionally produced in the photolysis has only two similar-intensity ν_{CO} bands at 1950 and 1830 cm^{-1}. This may correspond to an isomeric form of $W_2Cl_4(CO)_4(eHTP)$ that has the *same* coordination environment about each tungsten center.

The irradiation of $Mo_2(CO)_6(eHTP)$ appears to proceed in a manner similar to that seen for the tungsten analogue. After 5 days of photolysis a yellow solution is formed that occasionally has some yellow precipitate as well. The infrared spectrum of the soluble yellow species is nearly identical with that of $W_2Cl_4(CO)_4(eHTP)$ and shows four ν_{CO} bands at 1970, 1920, 1830, and 1810 cm^{-1} as well as peaks characteristic of eHTP. The one-dimensional ^{31}P NMR and two-dimensional ^{31}P–^{31}P COSY spectra of the molybdenum photoproduct are also quite similar to those for tungsten and are shown in Figure 4. The spectra clearly indicate the presence of two different molybdenum environments, as seen in the tungsten system. Peaks 1 and 2 represent the internal phosphorus atoms, while peaks 3 and 4 indicate the external phosphine groups on each half of the complex. The main difference between the ^{31}P NMR spectra for the Mo and W compounds is that peak 4 is shifted downfield from both peaks 1 and 2. On the basis of the spectral data, we propose that the soluble molybdenum photoproduct is $Mo_2Cl_4(CO)_4(eHTP)$ and has two different ligand environments about each metal center, as discussed above for the tungsten system. The yellow precipitate that occasionally forms (ν_{CO} = 1970, 1830 cm^{-1}) in the photolysis of $Mo_2(CO)_6(eHTP)$ would also appear to be an isomeric form of $Mo_2Cl_4(CO)_4(eHTP)$ in which each metal center has the same ligand geometry, just as was seen in the tungsten reaction.

The limited solubility of the starting $M_2(CO)_6(eHTP)$ compounds in essentially only CH_2Cl_2 limited the photochemical studies and led, perhaps not unexpectedly, to the chlorination reactions described. The difference between the Cr and Mo/W reaction pathways is consistent with the general chemistry of the related mononuclear systems, even though this is the first reported example of photochemical chlorinations using CH_2Cl_2 for producing seven-coordinate $MCl_2(CO)_2(P_3)$ type complexes. The apparent absence of any M–M cooperative interactions leads us to believe that we should concentrate our efforts on the binuclear reaction chemistry of lower coordinate later transition metal dimer complexes. The synthesis, characterization, and reactivity studies of group VIII dimers based on eHTP and tetratertiary phosphine ligand derivatives[24] will be reported in future papers.

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Supplementary Material Available: Infrared spectra for the yellow soluble and insoluble $M_2Cl_4(CO)_4(eHTP)$ (M = Mo, W) photoproducts and tables of crystal and data collection parameters, anisotropic thermal parameters, and all bond distances and angles for the W complex (8 pages); a listing of calculated and observed structure factors for $W_2(CO)_7(C_{19}H_{43}P_5)$ (9 pages). Ordering information is given on any current masthead page.

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Competing Formation of Bridging Diphenylphosphido and Bridging (Diphenylphosphino)cyclopentadienyl Ligands during the Reaction of $[M(CO)_5PPh_2]^-$ (M = Cr, Mo, W) with $CpRu(CO)_2Cl$. X-ray Structure of $(CO)_5W(\mu\text{-}C_5H_4PPh_2)Ru(CO)(\mu\text{-}CO)_2Ru(CO)Cp\cdot CH_2Cl_2$

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The reaction of $[M(CO)_5PPh_2]^-$ with $CpRu(CO)_2Cl$ (M = Cr, Mo, W) is highly dependent on the metal. When M = Mo or W, the products isolated are $(CO)_5M(\mu\text{-}C_5H_4PPh_2)Ru(CO)(\mu\text{-}CO)_2Ru(CO)Cp$ (M = Mo (**2**), W (**3**)). **3**·CH_2Cl_2 crystallizes in the triclinic space group C_i-$P\bar{1}$ with cell dimensions a = 12.184 (4) Å, b = 14.952 (2) Å, c = 9.545 (2) Å, α = 96.46 (1)°, β = 92.94 (2)°, γ = 77.39 (2)°, and Z = 2. The structure was solved and refined to R and R_w values of 0.044 and 0.056, respectively, by using 4813 reflections. Experimental results suggest that the first step of the formation of **2** and **3** is a nucleophilic attack of $[M(CO)_5PPh_2]^-$ on the cyclopentadienyl ligand of $CpRu(CO)_2Cl$.

Introduction

The synthesis of and the study of the reactivity of heterobimetallic complexes are now well-established areas of activity in organometallic chemistry.[1] Among the motivations for such study is the hope that combining metals with different chemical properties would lead to synergic effects and to new chemical reactivity. In this field, we are presently interested in the synthesis of heteropolymetallic systems associating group 6 and group 8 metals. Such systems associate metals with quite different properties, e.g. oxophilicity for group 6 and hydrogen activation for group 8, which

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could lead to interesting reducing properties for oxygen-containing organic molecules. We recently succeeded in the synthesis of new $[PPh_4][M(Ru_3(CO)_{12}]$ clusters (M = Mo or W),[2] but unfortunately, these compounds decompose under catalysis conditions.

Consequently, we have searched for more stable structures, and we thought that a possible way to stable heterodinuclear group 6–group 8 metal–metal complexes was through the use of bridging diphenylphosphido ligands. Indeed, these ligands exhibit two advantages: (i) they can help the synthesis by "bridging assistance",[1] and (ii) they can stabilize the dinuclear units, thus preventing or delaying fragmentation reactions.

From these two advantages derives the impressive number of phosphido-bridged complexes described in the literature,[3] even though there are now numerous examples indicating that $\mu\text{-}PR_2$ ligands are not always inert.

In this paper, we present the results of what we thought to be a possible approach of the complexes $(CO)_5M(\mu\text{-}PPh_2)Ru(CO)_2Cp$ (M = Cr, Mo, W), viz. reaction 1.

$$Li[(CO)_5MPPh_2] + RuCl(CO)_2Cp \rightarrow (CO)_5M(\mu\text{-}PPh_2)Ru(CO)_2Cp \quad (1)$$

Actually, the reaction proceeds in this way only when M = Cr, while for M = Mo or W, it leads to the formation of trinuclear complexes containing a (diphenylphosphino)cyclopentadienyl bridging ligand, $(CO)_5M(Ph_2PC_5H_4)Ru(CO)(\mu\text{-}CO)_2Ru(CO)Cp$, whose X-ray structure has been established for M = W.

Results and Discussion

The "bridged-assisted" method,[1] which has been applied with success for the synthesis of several examples of phosphido-bridged heterobimetallic complexes by Geoffroy et al.,[3c] was less successful than expected in the case of reaction 1 and more precisely metal-dependent.

When M = Cr, the reaction leads to an orange solution from which, after chromatography and crystallization, is isolated a yellow complex, **1**. Mass spectrometry and chemical analysis are consistent with the $CrRu(CO)_7(PPh_2)(Cp)$ formulation for **1**.

Infrared spectroscopy in the ν_{CO} region is consistent with the presence of one $Ru(CO)_2$ group and one $M(CO)_5$ group bonded to an unsymmetrical ligand, suggesting the $(CO)_5Cr(\mu\text{-}PPh_2)Ru(CO)_2Cp$ structure.

The ^1H and ^{31}P NMR data are also in agreement with this formulation, and ^1H resonances are observed for the Cp and PPh_2 ligands in a 5:10 intensity ratio. Confirmation of the proposed structure comes from the ^{31}P chemical shift (31.8 ppm) of the phosphido bridge, which implies that the Cr and Ru metallic centers are not bonded.[3a,5] When M = Mo or W, under the same reaction conditions as for M = Cr, the formation in low yield of a different type of complex, **2** (M = Mo) or **3** (M = W) is observed.

Evidence for the different nature of **2** and **3** comes first from infrared spectroscopy in the ν_{CO} stretching region, which shows spectra quite different from those of **1**.

Furthermore, the proton NMR spectra of **2** and **3** show, apart from phenyl resonances, one singlet and multiplets in a 5:4 ratio for the cyclopentadienyl hydrogens, with a phenyl to cyclopentadienyl proton ratio of 10:9. The ^{31}P NMR spectra show only one singlet at 25.3 ppm for **2** and 7.6 ppm for **3** with a J_{W-P} coupling constant of 252 Hz in the latter case, giving evidence that the PPh_2 group remains bonded to the tungsten atom. Mass spectrometry and chemical analysis are consistent with the $MRu_2(CO)_9PPh_2(C_{10}H_9)$ formulation.

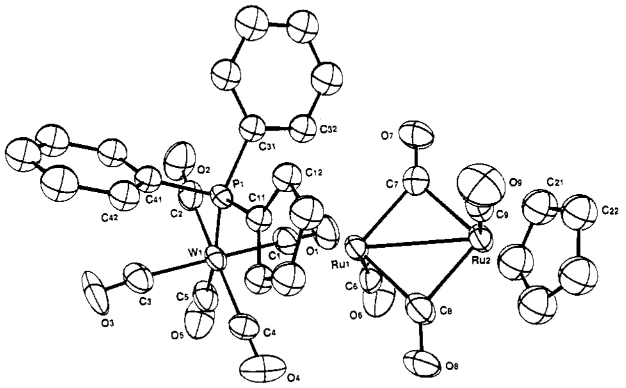

Figure 1. Structure of 3, showing the atomic numbering scheme.

Table I. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 3

Ru(1)···W(1)	5.005 (1)	Ru(1)–C(8)	2.04 (1)
W(1)–P(1)	2.536 (2)	Ru(2)–C(7)	2.054 (8)
W(1)–C(1)	2.01 (1)	Ru(2)–C(8)	2.02 (1)
W(1)–C(2)	2.02 (1)	Ru(2)–C(9)	1.886 (9)
W(1)–C(3)	2.05 (1)	P(1)–C(11)	1.814 (7)
W(1)–C(4)	2.02 (1)	P(1)–C(31)	1.814 (7)
W(1)–C(5)	1.97 (1)	P(1)–C(41)	1.828 (6)
Ru(1)–Ru(2)	2.746 (1)	⟨Ru(1)–C(Cp)⟩	2.28 [2]
Ru(1)–C(6)	1.866 (9)	⟨Ru(2)–C(Cp)⟩	2.26 [1]
Ru(1)–C(7)	2.03 (1)	⟨C–O⟩[a]	1.15 [3]
P(1)–W(1)–C(1)	94.8 (3)	C(8)–Ru(2)–C(9)	92.9 (4)
P(1)–W(1)–C(2)	87.8 (3)	W(1)–P(1)–C(11)	109.7 (2)
P(1)–W(1)–C(3)	88.2 (3)	W(1)–P(1)–C(31)	115.5 (2)
P(1)–W(1)–C(4)	95.4 (3)	W(1)–P(1)–C(41)	122.2 (2)
P(1)–W(1)–C(5)	174.3 (3)	C(7)–Ru(1)–C(8)	95.3 (4)
C(1)–W(1)–C(2)	88.0 (4)	Ru(1)–Ru(2)–C(7)	47.3 (3)
C(1)–W(1)–C(3)	176.9 (4)	Ru(1)–Ru(2)–C(8)	47.9 (3)
C(1)–W(1)–C(4)	90.2 (4)	Ru(1)–Ru(2)–C(9)	93.8 (2)
C(1)–W(1)–C(5)	88.5 (5)	C(7)–Ru(2)–C(8)	95.2 (4)
C(2)–W(1)–C(3)	91.0 (4)	C(7)–Ru(2)–C(9)	93.6 (4)
C(2)–W(1)–C(4)	176.5 (4)	C(11)–P(1)–C(31)	102.1 (3)
C(2)–W(1)–C(5)	87.7 (4)	C(11)–P(1)–C(41)	101.2 (3)
C(3)–W(1)–C(4)	90.6 (4)	C(31)–P(1)–C(41)	103.9 (3)
C(3)–W(1)–C(5)	88.4 (4)	Ru(1)–C(7)–Ru(2)	84.5 (3)
C(4)–W(1)–C(5)	89.2 (4)	Ru(1)–C(7)–O(7)	138.8 (8)
Ru(2)–Ru(1)–C(6)	90.1 (2)	Ru(2)–C(7)–O(7)	136.6 (8)
Ru(2)–Ru(1)–C(7)	48.1 (2)	Ru(1)–C(8)–Ru(2)	85.0 (4)
Ru(2)–Ru(1)–C(8)	47.1 (3)	Ru(1)–C(8)–O(8)	137.4 (9)
C(6)–Ru(1)–C(7)	90.6 (4)	Ru(2)–C(8)–O(8)	137.3 (9)
C(6)–Ru(1)–C(8)	88.2 (4)	⟨Ru–C–O⟩[a]	177 [2]

[a] Within carbonyl ligands except C(7)O(7) and C(8)O(8).

All of these results suggest that a modification of one Cp ligand has occurred. To elucidate further the structure of **2** and **3**, an X-ray structure determination was undertaken for **3**.

An ORTEP plot of **3** is shown in Figure 1, and bond lengths and angles of interest are shown in Table I. **3** is a trinuclear complex formed by a dinuclear $Ru_2(CO)_2(\mu\text{-}CO)_2$ unit, with Ru(2) bonded to a cyclopentadienyl ligand and Ru(1) linked to a $W(CO)_5$ unit through a (diphenylphosphino)cyclopentadienyl ligand.

So, it appears that **3** is the result of a complex reaction implying the formation of a (diphenylphosphino)cyclopentadienyl ligand and the coupling of two $CpRu(CO)_2$ units. **3** provides further examples of the bridging capability of the (diphenylphosphino)cyclopentadienyl ligand, a fact well illustrated by other observations during the last few years.[6]

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The dinuclear ruthenium unit of **3** closely resembles that of $[CpRu(CO)_2]_2$[7] and $[(C_5Me_4Et)Ru(CO)_2]_2$.[8] It consists of two Ru atoms at a bonding distance of 2.746 (1) Å bridged by two carbonyl groups and bonded to two terminal carbonyl ligands that are in a trans position relative to the Ru(1)–C(7)–Ru(2)–C(8) plane. Even though Ru(2) is bonded to a cyclopentadienyl ligand and Ru(1) is bonded to a $PPh_2C_5H_4$ ligand, the Ru–C distances for the Ru(CO) bridging or terminal groups are nearly the same around Ru(1) and Ru(2) and similar to those found in $[CpRu(CO)_2]_2$[7] or $[(C_5Me_4Et)Ru(CO)_2]_2$.[8] The $Ru(C_5H_5)$ or $Ru(C_5H_4PPh_2)$ distances also are very similar.

Considering now the $(CO)_5WPPh_2C_5H_4$ part of the molecule, the geometry around W(1) is a slightly distorted octahedron, with P(1)–W(1)–C(1) and P(1)–C(1)–C(4) angles greater than 90° due to steric interactions with the $C_5H_4PPh_2$ ligand. This effect is also apparent for the *trans*-C-W-C or *trans*-P-W-C angles, which are slightly smaller than 180°. The W(1)–P(1) bond length is in the normal range for a $W–PR_3$ distance[9] while the W(1)–C(5) distance is the shortest of the W–(CO) bonds, as expected.

The W(1)–P(1)–C(11) angle (109.7 (2)°) is between the values found in $CpTiCl_2[\mu\text{-}C_5H_4PPh_2]MnCp(CO)_2$[6b] (116.3 (5)°) and $(CO)_3Mo[\mu\text{-}(C_5H_4)PPh_2]MnCp(CO)_2$[6a] (103.6 (2)°) complexes. The overall geometry around phosphorus is also very similar to that found in these two complexes.

To summarize, compounds **2** and **3** appear as the result of a complex reaction implying ring substitution on the cyclopentadienyl ligand by the $M(CO)_5PPh_2$ entity and coupling with a second $CpRu(CO)_2$ entity. The reactivity of $CpFeL_1L_2X$ with anionic reagents provides several examples of such type of reactions, implying direct attack of the anionic reagent on the ring[10] or migration of X ($X = SiR_3$) onto the ring[11] induced by strong bases.

To gain insight into the mechanism of formation of **2** and **3**, we have done two experiments.

In one experiment, the order of introduction of the reactants was reversed and the solution of $[M(CO)_5PPh_2]^-$ was slowly added to the solution of $CpRu(CO)_2Cl$. We thus hoped that if ring substitution occurred through the initial formation of $CpRu(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ followed by a migration induced by an excess of anionic reagent, then the formation of **2** and **3** would be prevented or reduced. Unfortunately, no changes were observed in the product distribution.

In a second experiment, we reacted **1** with $[W(CO)_5PPh_2]^-$. No reaction occurred.

Both results strongly suggest that the first step of the formation of **2** and **3** is nucleophilic attack of the $[M(CO)_5PPh_2]^-$ anions (M = Mo, W) on the cyclopentadienyl ring of $CpRu(CO)_2Cl$, leading to the $[(CO)_5M(\mu\text{-}PPh_2C_5H_5)Ru(CO)_2Cl]^-$ intermediates. The fact that compounds **2** and **3** are the main products of the reaction for M = Mo or W can be attributed to the increase in nucleophilicity of phosphido anion complexes passing from M = Cr to M = W (trace amounts of the equivalents of **2** and **3** when M = Cr and of **1** when M = Mo or W have been detected by chromatography and identified by their infrared spectra). Although **3** has bridging carbonyl groups in the solid state, its infrared spectrum in solution (hexane) shows the presence of such bridging ligands only upon very careful examination. Indeed, a very weak band is observed in hexane solution at 1802 cm^{-1}, whereas in KBr pellets a bridging CO absorption band is observed at 1785 cm^{-1}. The same phenomenon is observed with **2** where a very weak band at 1805 cm^{-1} is detected in hexane solution. In the solid state, a bridging CO group absorption band is observed at 1785 cm^{-1}. This suggests that, as for the $[CpRu(CO)_2]_2$ dimer,[12,13] in solution there is an equilibrium between bridged and nonbridged forms of **2** and **3**.

Table II. Crystallographic Data for Compound $3\cdot CH_2Cl_2$

chem formula: $C_{32}H_{21}Cl_2O_9PRu_2W$	fw: 1037.4
	space group: C_i^1-$P\bar{1}$
$a = 12.184$ (4) Å	$T = 22$ °C
$b = 14.952$ (2) Å	$\lambda = 0.7093$ Å
$c = 9.545$ (2) Å	$\rho_{calcd} = 1.876$ g cm^{-3}
$\alpha = 96.46$ (1)°	$\mu = 44.40$ cm^{-1}
$\beta = 92.94$ (2)°	transmissn factors:[a] 0.506–0.998
$\gamma = 77.39$ (2)°	$R(F_o) = 0.044$
$V = 1685.6$ Å^3	$R_w(F_o) = 0.056$
$Z = 2$	

[a] Ψ-Scan method.

To gain further insight into this phenomenom of fluxionality, we have performed a proton NMR variable-temperature study of **2** and **3**. As for $[CpRu(CO)_2]_2$,[13] no change of the Cp resonance is observed from room temperature to 203 K.

These results bring no further information about the fluxionality of **2** and **3**, but infrared data suggest that the mechanism is similar to the case of the $[CpRu(CO)_2]_2$ compound.

Experimental Section

General Data. All reactions were performed under an atmosphere of argon by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer. ^1H and ^{31}P NMR spectra were recorded with a Bruker WH90 spectrometer and variable-temperature experiments were performed with a Bruker AC200. Mass spectra have been obtained on a Varian MAT311A instrument.

The $M(CO)_5(PPh_2H)$ complexes were synthesized by starting either from $M(CO)_5THF$ or from $[NEt_4][M(CO)_5Br]$,[14] the latter giving the best yields (~90%). They were identified by comparison of their spectroscopic data with published values.[15] $CpRu(CO)_2Cl$ was obtained by the reaction of carbon tetrachloride with $CpRu(CO)_2H$[16] and isolated in 68% yield.

Synthesis of $(CO)_5Cr(\mu\text{-}PPh_2)Ru(CO)_2Cp$ (1). $Cr(CO)_5(PPh_2H)$ (0.33 g, 0.86 mmol) was dissolved in 10 mL of THF. The solution was cooled to 0 °C, and a 10% excess of *n*-BuLi in hexane was slowly added. The solution turned orange yellow. $CpRu(CO)_2Cl$ (0.22 g, 0.86 mmol) was then added. The solution turned orange and was stirred for 10 min at 0 °C and 10 min at room temperature. The solution was evaporated to dryness, and the residue was chromatographed on a Florisil column. Elution with toluene/hexane (40/60) gave a yellow band. Evaporation of the solvent and crystallization in a dichloromethane/methanol afforded 130 mg (25% yield) of **1** as yellow crystals. Anal. Calcd for $C_{24}H_{15}O_7PCrRu$: C, 48.08; H, 2.50. Found: C, 47.85; H, 2.25. Mass spectrometry: $m/z = 600$ (^{52}Cr, ^{102}Ru). IR ν_{CO} (hexane solution): 2053 m, 2030 m, 1988 m, 1978 w, 1938 s, 1926 s, 1915 s cm^{-1}. ^1H NMR ($CDCl_3$): 7.64–7.30 (m) (C_6H_5), 5.08 (s) (C_5H_5) ppm. ^{31}P NMR ($CDCl_3$): 31.8 ppm.

Synthesis of $Ru_2M(C_5H_4PPh_2)(Cp)(CO)_9$ (M = Mo (2), W (3)). The $[M(CO)_5PPh_2]^-$ anions (M = Mo, W) were prepared by the procedure outlined for the chromium analogue starting from $Mo(CO)_5(PPh_2H)$ (0.33 g, 0.78 mmol) or from $W(CO)_5(PPh_2H)$ (0.59 g, 1.16 mmol). An equimolecular quantity of $CpRu(CO)_2Cl$ was added at 0 °C, and the mixture was stirred for 10 min at 0 °C and 10 min at 20 °C.

The resulting orange solution was evaporated to dryness, and the residue was chromatographed on a Florisil column. Elution with a 40/60 mixture of toluene/hexane gave successively traces of $M(CO)_5PPh_2H$, identified by infrared spectroscopy, and a yellow band. Evaporation of the solvent and crystallization in a dichloromethane/hexane afforded the product.

For M = Mo, 0.07 g of **2** was obtained as yellow crystals (10.3% yield). Anal. Calcd for $C_{31}H_{19}O_9PMoRu_2$: C, 42.95; H, 2.19. Found: C, 43.09; H, 2.28. Mass spectrometry: $m/z = 868$ (^{98}Mo, ^{102}Ru). IR ν_{CO} (hexane solution): 2071 m, 2020 w, 2010 w, 1981 s, 1955 vs, 1803

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Table III. Final Atomic Coordinates and U_{eq} or U_{iso} Values (Å^2 × 100) for Compound **3**

atom	x/a	y/b	z/c	U_{eq} or U_{iso}
W(1)	0.95021 (3)	0.35993 (2)	0.25807 (3)	3.83 (3)
Ru(1)	0.74077 (5)	0.20263 (4)	−0.12352 (7)	3.40 (4)
Ru(2)	0.67097 (6)	0.04347 (5)	−0.21952 (7)	3.73 (4)
P(1)	0.7561 (2)	0.4001 (1)	0.1425 (2)	3.3 (1)
C(1)	0.930 (1)	0.2399 (8)	0.317 (1)	6.0 (6)
O(1)	0.9219 (7)	0.1703 (6)	0.356 (1)	8.3 (6)
C(2)	0.8811 (9)	0.4226 (7)	0.441 (1)	5.4 (6)
O(2)	0.8395 (9)	0.4542 (7)	0.5460 (9)	8.6 (7)
C(3)	0.9780 (9)	0.4822 (8)	0.206 (1)	5.9 (6)
O(3)	0.9993 (8)	0.5451 (6)	0.171 (1)	9.5 (6)
C(4)	1.0270 (8)	0.2926 (7)	0.082 (1)	5.3 (6)
O(4)	1.0723 (8)	0.2513 (8)	−0.020 (1)	9.3 (7)
C(5)	1.0970 (8)	0.3408 (7)	0.359 (1)	6.3 (6)
O(5)	1.1848 (7)	0.3301 (6)	0.416 (1)	9.1 (6)
C(6)	0.8565 (8)	0.1356 (6)	−0.017 (1)	4.6 (5)
O(6)	0.9275 (7)	0.0946 (5)	0.046 (1)	7.8 (5)
C(7)	0.6283 (8)	0.1392 (6)	−0.0485 (9)	4.4 (5)
O(7)	0.5684 (7)	0.1495 (6)	0.0453 (9)	7.2 (5)
C(8)	0.7859 (9)	0.1054 (8)	−0.291 (1)	5.4 (6)
O(8)	0.8543 (8)	0.0888 (7)	−0.3787 (9)	8.9 (6)
C(9)	0.5548 (8)	0.1034 (6)	−0.336 (1)	4.7 (5)
O(9)	0.4893 (7)	0.1344 (7)	−0.410 (1)	7.4 (6)
C(11)	0.7248 (4)	0.3518 (5)	−0.0348 (5)	3.6 (2)
C(12)	0.6165 (4)	0.3420 (5)	−0.0877 (5)	4.1 (2)
C(13)	0.6232 (4)	0.3177 (5)	−0.2357 (5)	5.2 (2)
C(14)	0.7356 (4)	0.3124 (5)	−0.2742 (5)	5.2 (2)
C(15)	0.7984 (4)	0.3335 (5)	−0.1500 (5)	4.4 (2)
C(21)	0.6607 (7)	−0.0694 (6)	−0.0828 (6)	6.9 (3)
C(22)	0.6129 (7)	−0.0903 (6)	−0.2181 (6)	6.4 (3)
C(23)	0.6984 (7)	−0.1032 (6)	−0.3185 (6)	7.3 (3)
C(24)	0.7991 (7)	−0.0902 (6)	−0.2453 (6)	7.9 (3)
C(25)	0.7758 (7)	−0.0693 (6)	−0.0996 (6)	7.5 (3)
C(31)	0.6418 (4)	0.3803 (3)	0.2412 (7)	4.2 (2)
C(32)	0.6526 (4)	0.2932 (3)	0.2865 (7)	4.8 (2)
C(33)	0.5665 (4)	0.2740 (3)	0.3612 (7)	6.6 (3)
C(34)	0.4698 (4)	0.3418 (3)	0.3907 (7)	6.3 (3)
C(35)	0.4591 (4)	0.4289 (3)	0.3455 (7)	6.7 (3)
C(36)	0.5451 (4)	0.4481 (3)	0.2707 (7)	5.2 (2)
C(41)	0.7185 (6)	0.5235 (4)	0.1242 (4)	3.9 (2)
C(42)	0.7010 (6)	0.5570 (4)	−0.0076 (4)	4.6 (2)
C(43)	0.6789 (6)	0.6517 (4)	−0.0171 (4)	6.2 (3)
C(44)	0.6743 (6)	0.7129 (4)	0.1051 (4)	5.9 (2)
C(45)	0.6919 (6)	0.6794 (4)	0.2369 (4)	5.8 (3)
C(46)	0.7140 (6)	0.5847 (4)	0.2465 (4)	4.8 (2)
C	0.872 (2)	−0.046 (1)	0.332 (2)	5 (1)
Cl(1)	0.8826 (6)	−0.1618 (5)	0.3544 (7)	8.2 (4)
Cl(2)	0.7333 (7)	0.0117 (6)	0.2930 (8)	8.8 (5)

w cm^{-1}. IR ν_{CO} (acetonitrile solution): 2072 m, 2010 sh, 2001 s, 1970 sh, 1948 vs, 1790 sh, 1788 m cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.65 m (C_6H_5), 5.66 m (C_5H_4), 5.50 (C_5H_5) ppm. ^{31}P NMR ($CDCl_3$): 25.3 ppm.

For M = W, 0.05 g of **3** was obtained as yellow crystals (10.4% yield). Anal. Calcd for $C_{31}H_{19}O_9PWRu_2\cdot CH_2Cl_2$: C, 36.96; H, 2.01. Found: C, 37.96; H, 2.04. Mass spectrometry: m/z = 954 (^{184}W, ^{102}Ru). IR ν_{CO} (hexane solution): 2069 m, 2021 w, 2010 w, 1979 s, 1955 sh, 1945 vs, 1801 w cm^{-1}. IR ν_{CO} (acetonitrile solution): 2070 m, 2012 sh, 2002 s, 1970 sh, 1940 vs, 1795 sh, 1789 m cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.67 m (C_6H_5), 5.68 m (C_5H_4), 5.51 s (C_5H_5) ppm. ^{31}P NMR ($CDCl_3$): 7.6 ppm (J_{WP} = 252 Hz).

X-ray Structure Determination of 3·CH_2Cl_2. Crystals of **3** suitable for X-ray diffraction were obtained through recrystallization from dichloromethane/hexane at 18 °C. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range 24° $< 2\theta$(Mo Kα_1) $<$ 28°. Data reductions were carried out by using the SDP crystallographic computing package.[17] Table II presents further crystallographic information. Intensities of four standard reflections [1,−3,−5], [3,3,−6], [5,2,4], [5,−3,3] were measured every 2 h and showed a total loss in intensity of 7.1% from which data were corrected.

The structure was solved and refined by using a combination of the SDP crystallographic computing package[17] and the SHELX-76 package.[18] The positions of W, Ru, and P atoms were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses.

Atomic scattering factors were taken from the usual tabulations.[19] Anomalous dispersion terms for W, Ru, Cl, and P atoms were included in F_c.[20] An empirical absorption correction was applied.[21] The final refinements were conducted by using the SHELX-76 program. All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of phenyl rings and the cyclopentadienyl ring, which were refined as isotropic rigid groups in order to reduce the number of variable parameters (C_6H_5, C–C = 1.395 Å; C_5H_5 and C_5H_4, C–C = 1.420 Å). Hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart et al.[22]

Final atomic coordinates and U_{eq} × 100 (or U_{iso} × 100) for non-hydrogen atoms are given in Table III.

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Supplementary Material Available: Table S1 (anisotropic thermal parameters for **3**) and Table S2 (complete experimental data for the X-ray study of **3**) (3 pages); Table S3 (structure factor amplitudes (×10) for **3**) (24 pages). Ordering information is given on any current masthead page.

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(23) See paragraph at end of paper regarding supplementary material.