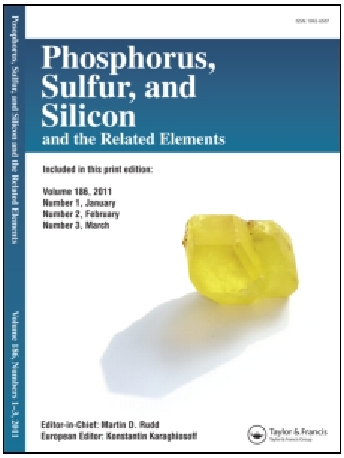


Phosphorus, Sulfur, and Silicon
and the Related Elements

Included in this print edition:
Volume 186, 2011
Number 1, January
Number 2, February
Number 3, March

Editor-in-Chief: Martin D. Rudd
European Editor: Konstantin Karaghiosoff

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIVITY OF [$M_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)$] (M = Ru, Os) TOWARDS ORGANIC AND ORGANOMETALLIC ELECTROPHILES; EVIDENCE FOR ELECTROPHILIC *endo*-ATTACK AT THE PHOSPHIDO MOIETY OF [$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)$]

Lutz Heuer[ab]; Ebbe Nordlander[ac]; Brian F. G. Johnson[d]; Jack Lewis[a]; Paul R. Raithby[a]
[a] University Chemical Laboratory, Cambridge, U. K. [b] Bayer AG, Werk Urdingen, Business Unit Organic Chemicals, Krefeld, Federal Republic of Germany [c] Inorganic Chemistry 1, Chemical Center, Lund University, Lund, Sweden [d] Department of Chemistry, University of Edinburgh, Edinburgh, U. K.

To cite this Article Heuer, Lutz , Nordlander, Ebbe , Johnson, Brian F. G. , Lewis, Jack and Raithby, Paul R.(1995) 'REACTIVITY OF [$M_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)$] (M = Ru, Os) TOWARDS ORGANIC AND ORGANOMETALLIC ELECTROPHILES; EVIDENCE FOR ELECTROPHILIC *endo*-ATTACK AT THE PHOSPHIDO MOIETY OF [$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)$]', Phosphorus, Sulfur, and Silicon and the Related Elements, 103: 1, 241 — 252

To link to this Article: DOI: 10.1080/10426509508027383

URL: http://dx.doi.org/10.1080/10426509508027383

Phosphorus, Sulfur, and Silicon, 1995, Vol. 103, pp. 241–252
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIVITY OF $[M_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (M = Ru, Os) TOWARDS ORGANIC AND ORGANOMETALLIC ELECTROPHILES; EVIDENCE FOR ELECTROPHILIC *endo*-ATTACK AT THE PHOSPHIDO MOIETY OF $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$

LUTZ HEUER,[†,1] EBBE NORDLANDER,[*,†,2] BRIAN F. G. JOHNSON,[*,‡]
JACK LEWIS,[*,†] and PAUL R. RAITHBY[†]
†*University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.;*
‡*Department of Chemistry, University of Edinburgh, King's Buildings,*
West Mains Road, Edinburgh EH9 3JJ, U.K.

Dedicated to Professor R. Schmutzler on the occasion of his 60th birthday

(Received November 14, 1994; in final form February 4, 1995)

Electrophilic attack on the bridging phosphido moiety of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**1**) allows the formation of new phosphorus-containing compounds. The phosphido clusters $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PHR)]$ (R = $(CH_2)_6I$ (**2a**), $(CH_2)_{10}I$ (**2b**), C_4H_8OH (**2c**), $HOs_3(CO)_{10}(PPh_3)$ (**4a**), $HOs_3(CO)_{10}\{P(OMe)_3\}$ (**4b**)) have been synthesized by the reaction of **1** with the appropriate electrophiles. When R = alkyl, both *exo*- and *endo*-isomers are formed. The formation of both isomers indicates that *endo*-attack plays a significant role in these reactions. When R = $(\mu\text{-}H)Os_3(CO)_{10}(PR_3)$ the *exo*-isomers are the exclusive products. Reaction of the ruthenium analogue of **1** with $[Os_3(CO)_{10}(NCMe)]$ leads to the formation of $[Ru_3Os_3(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}P)]$ (**6**). The crystal structure of $[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)]$ (**4b**) is presented.

Key words: Phosphido moiety, cluster, Osmium, Ruthenium, electrophilic attack, isomer.

INTRODUCTION

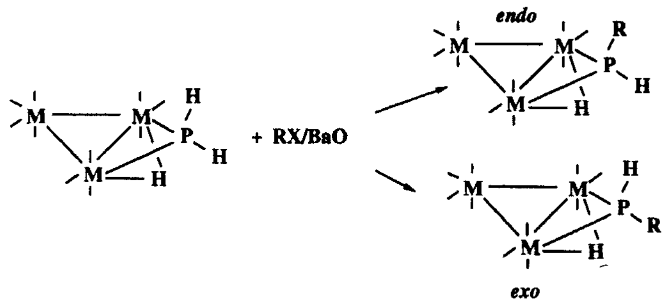
Transition metal carbonyl clusters can function as catalysts for petrochemical reactions[3,4] but are often plagued by fragmentation when subjected to the conditions employed in industrial chemical reactions. There is therefore considerable interest in using main group elements as bridges between metal fragments in the build-up of metal clusters of intermediate and high nuclearities.[5] Phosphorus has been used extensively in this context; phosphido-bridges are especially prevalent, but phosphinidenes are also common and several clusters containing semi-interstitial and interstitial phosphorus atoms are known.[6,7] It has been recognized that the phosphorus-metal bond strength in these bridged, capped or interstitial compounds is often substantially stronger than those of the metal-metal and metal-carbonyl bonds, and that the phosphorus ligand may thus stabilize the clusters.[8] In an effort to develop rational synthetic pathways to such phosphorus-containing compounds, we have investigated the reactivity of transition metal carbonyl clusters containing phosphido- and phosphinidene-moieties.

Addition of the appropriate phosphine R-PH_2 (R = alkyl, aryl) to trinuclear ruthenium or osmium clusters affords phosphido-bridged clusters of the general formula $[M_3(\mu\text{-H})(CO)_{10}(\mu\text{-PRH})]$ (M = Ru, Os).[9-11] It has been found that such compounds generally exhibit the sterically favoured *exo* geometry with respect to the coordination of the substituent R to the phosphorus atom. We have previously shown that the phosphorus-coordinated protons of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-PH}_2)]$ (**1**) are relatively acidic and that it may be reacted with electrophiles to form both *exo*- and *endo*-isomers.[12] Here, we wish to report further investigations into the reactions of **1** with electrophilic organic and new organometallic reagents.

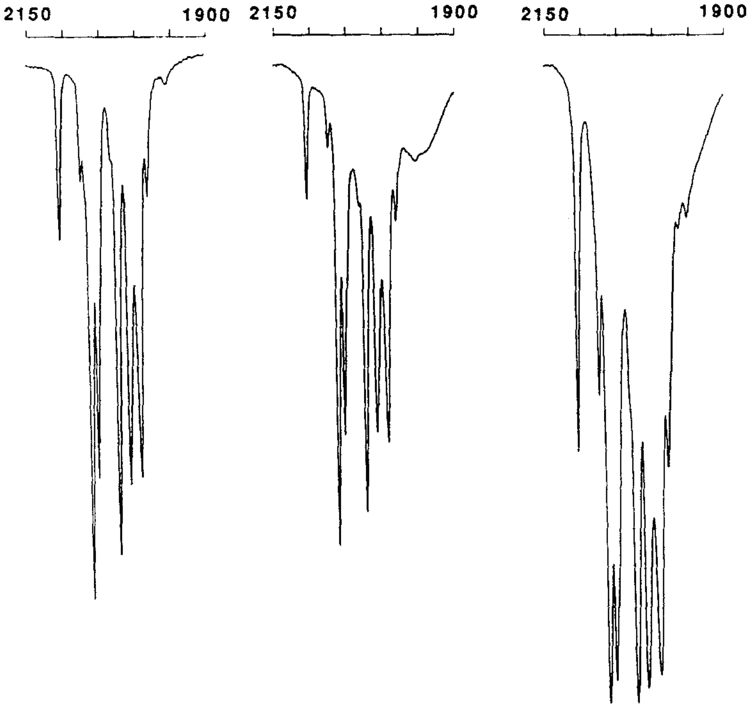
RESULTS AND DISCUSSION

The presence of the mild base BaO in a relatively large excess promotes the reaction of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-PH}_2)]$ (**1**) with electrophilic reagents, presumably through further deprotonation of the phosphorus atom.[12] Thus, the reaction of **1** with RI (R = $(CH_2)_6I$, $(CH_2)_{10}I$) and BaO proceeds smoothly to produce the corresponding phosphorus-substituted products $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-PHR})]$ (R = $(CH_2)_6I$ (**2a**), $(CH_2)_{10}I$ (**2b**)) which are obtained in both *exo*- and *endo*-isomeric forms (Scheme I). In all reactions, diiodohexane/-decane was used in excess and there was no evidence for the formation of dimers through the reaction of one equivalent of diiodohexane/-decane with two equivalents of **1**. The reaction of **1** with an excess of 1-butane-epoxide followed by work-up in acidified dichloromethane results in the formation of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-PH}(C_4H_8OH))]$ (**2c**).

Compounds **2a–2c** have been characterized by IR and NMR spectroscopy as well as mass spectroscopy (Figure 1, Table I). Comparison of the IR and NMR spectroscopic data of the new compounds with those of the clusters $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-PHPh})]$ or $[Ru_3(\mu\text{-H})(CO)_{10}(\mu\text{-PHPh})]$, which are known to possess *exo*-geometries on the basis of single crystal X-ray structure analyses,[13] has permitted us to assign the structures of **2a–c**. We have tested our assignments of *exo* and *endo* protons through the comparison of their ^{1}H-NMR spectra in $CDCl_3$ to the equivalent spectra obtained in d_6-benzene as solvent. The phosphorus-coordinated proton of the *endo* isomer undergoes the more substantial solvent shift.



SCHEME I Formation of *exo* and *endo* isomers of $[M_3(\mu\text{-H})(CO)_{10}(\mu\text{-PHR})]$. Note: In a previous publication (Reference 12) we have defined *exo* and *endo* with respect to the proton. Here we use the conventional definition, *i.e.* with respect to the substituent R.



2a **2b** **2c**

FIGURE 1 Solution infra-red spectra (hexane, $\nu_{C—O}$ region) of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PHR)]$ (R = $(CH_2)_6I$ (**2a**), $(CH_2)_{10}I$ (**2b**), C_4H_8OH (**2c**)).

In all solvents used, it is the corresponding proton of the *exo* isomer that shows the larger coupling ($^3J_{H—H}$) to the hydrido-ligand. Based on integration of the hydride resonances in the ^{1}H-NMR spectra, it is found that the ratios of the *exo*/*endo* isomers are approximately 20:80 for compounds **2a** and **b** and *ca*. 25:75 for **2c**. The fact that *endo* isomers are detected implies that the electrophilic attack at the phosphorus atom is mainly *endo*, and that the sterically (thermodynamically) favoured *exo* form is formed by isomerization from the (kinetically) favoured *endo* form.

The relative acidity of the phosphorus-coordinated protons of **1** has been explored for the linkage of clusters *via* phosphidene bridges.[9] All crystal structures of such phosphinidene-linked compounds show that the *exo*-type isomer is formed. To further probe this reactivity, we have synthesized the clusters $[Os_3(CO)_{10}(PR_3)(NCMe)]$ (R = Ph (**3a**), OMe (**3b**)) which may serve as (precursors for) organometallic electrophiles. Clusters **3a** and **b** are obtained by reacting the appropriate mono-substituted trinuclear Os clusters $[Os_3(CO)_{11}(PR_3)]$ with Me_3NO in the presence of acetonitrile. Mild thermolysis of **1** in the presence of stoichiometric equivalents of **3a** or **b** results in the formation of $[Os_6(\mu\text{-}H)_2(CO)_{20}(PR_3)(\mu_3\text{-}PH)]$ (R = Ph (**4a**), OMe (**4b**), Scheme II) which have been characterized by IR and NMR spectroscopy, mass spectroscopy and, in the case of **4b**, single crystal

TABLE I

Spectroscopic data for new compounds (*exo* and *endo* refers to isomers as defined in Scheme I)

Complex	IR (ν_{C-O})	^{1}H NMR (δ (ppm), J)[c]	^{31}P NMR (δ (ppm), J)[d]	MS (m/z, amu)[c] obsd.	MS (m/z, amu)[c] calcd.
2a $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH((CH_2)_6I))]$	2105 m, 2075 w, 2062 vs, 2053 s, 2024 vs, 2009 s, 1993 s, 1982 m[a]	6.02 (dm, $^1J_{P-H} \approx 402$, P**H**) 3.18 (t, $J_{H-H} \approx 7$, $PCH_2(CH_2)_5I$) 2.10–1.42 (m, $J_{H-H} \approx 7$, $PCH_2(\mathbf{CH_2})_5I$) −18.80 (dd, $^2J_{P-H} \approx 16$, $^3J_{H-H} \approx 4$, Os**H**, *endo*) −19.50 (dd, $^2J_{P-H} \approx 16$, $^3J_{H-H} \approx 4$, Os**H**, *exo*)		1100	1099
2b $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH((CH_2)_{10}I))]$	2103 m, 2074 w, 2061 vs, 2052 s, 2022 vs, 2008 s, 1993 s, 1981 m[a]	6.26 (d't', $^1J_{P-H} \approx 355$, $^3J_{H-H} \approx 7$, p**H**, *endo*) 6.05 (ddt, $^1J_{P-H} \approx 377$, $^3J_{H-H} \approx 7$, P**H**, *exo*) 3.16 (t, $J_{H-H} \approx 7$, $P\mathbf{CH_2}(CH_2)_9I$) 1.80–1.33 (m, $PCH_2(\mathbf{CH_2})_9I$) −19.00 (dd, $^2J_{P-H} \approx 15$, $^3J_{H-H} \approx 1$, Os**H**, *endo*) −19.55 (dd, $^2J_{P-H} \approx 16$, $^3J_{H-H} \approx 4$, Os**H**, *exo*)		1156	1155
2c $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH(C_4H_8OH))]$	2104 m, 2074 w, 2061 vs, 2052 s, 2023 vs, 2008 s 1992 s, 1981 m[a]	6.36 (ddt, $^1J_{P-H} \approx 415$, $^3H_{H-H} \approx 9$, $^3J_{H-H} \approx 7$, P**H**) 3.82 (m, **C**H(OH)) 2.10–1.80 (m, n($\mathbf{CH_2}$)) 0.99 (t, $C_3H_5(OH)\mathbf{CH_3}$) −19.52 (dd, $^2J_{P-H} \approx 16$, $^3J_{H-H} \approx 4$, Os**H**, *endo*) −21.36 (d, $^2J_{P-H} \approx 10$, Os**H**, *exo*)	−198.8 (d(br), $^1J_{P-H} \approx 411$)		

3a $[Os_3(CO)_{10}(PPh_3)(NCMe)]$	2081 w, 2030 s, 2017 ms, 1992 s, 1958^b	7.54–7.38 (m, $P(C_6\mathbf{H}_5)_3$), 2.58 (s, Os—$NCC\mathbf{H}_3$),		1159	1159
3b $[Os_3(CO)_{10}\{P(OMe)_3\}(NCMe)]$	2086 m, 2031 s, 2020 ms, 1996 s, 1968 ms^b	3.64 (d, $^3J_{P-H} \approx 7.7$, $P(OC\mathbf{H}_3)_3$), 2.67 (s, Os-$NCC\mathbf{H}_3$)	−34.4 (s, $\mathbf{P}(OCH_3)_3$)	1021	1021
4a $[Os_6(\mu\text{-}H)_2(CO)_{20}(PPh_3)(\mu_3\text{-}PH)$	2113 w, 2093 m, 2076 m, 2049 vs, 2040 ms, 2012 s, 1985 (sh)^b	7.86–7.28 (m, $P(C_6\mathbf{H}_5)_3$), 6.29 (d't'(ddd), $^1J_{P-Ha} \approx 384$, $^3J_{Ha-Hb} \approx {}^3J_{Ha-Hc} \approx 4$, P**H**) −17.95 (dd, $^2J_{P-Hb} \approx 14$, $Os\mathbf{H}_b$) −19.83 (ddd, $^2J_{PPh3-Hc} \approx$ $^2J_{P-Hc} \approx 11$ $Os\mathbf{H}_c$)			
4b $[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)]$	2119 w, 2094 m, 2076 m, 2051 vs, 2041 s, 2035 s, 2012 s, 1999 m 1988 m(sh), 1975 m(sh)^b	6.14 (d't'(ddd), $^1J_{P-Ha} \approx 328$, $^3J_{Ha-Hb} \approx {}^3J_{Ha-Hc} \approx 4$, P**H**) 3.79 (d, $^3J_{P-H} \approx 12.8$, $P(OC\mathbf{H}_3)_3$), −17.92 (dd, $^2J_{P-Hb} \approx 14$, $Os\mathbf{H}_b$) −19.83 (ddd, $^2J_{PO(CH3)3-Hc} \approx 8$, $2J_{P-Hc} \approx 12$ $Os\mathbf{H}_c$)	−50.5 (s, $\mathbf{P}(OCH_3)_3$), −330.2 (d, $^1J_{P-Ha} \approx 330$)	1870	1870
6 $[Ru_3Os_3(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}P)]$	2141 w, 2101 m, 2088 m, 2061 vs, 2033 vs, 2014 s, 1997 s^b		85.2 (dt, $^1J_{P-H} \approx 12, 11$, μ_4-**P**)	1473	1448 (M^+-CO)

[a] Hexane.

[b] CH_2Cl_2.

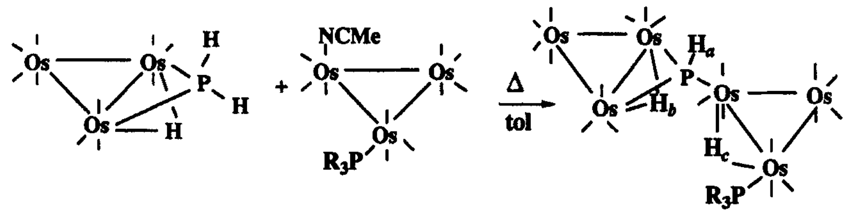
[c] $CDCl_3$, $SiMe_4$: $\delta = 0$.

[d] $CDCl_3$, $P(OMe)_3$: $\delta = 0$, downfield positive.

[e] Based on Os = 192.

X-ray crystallography. The ^{1}H and ^{31}P NMR spectra of **4a**, **b** are very similar to those of the *exo* isomer $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$, whose structure has been determined by X-ray crystallography, with the exception that additional splitting of the hydride H_c—due to coupling to the adjacent phosphine/phosphite ligand—is observed. The magnitude of the coupling constants is consistent with two *cis* $^{2}J_{P—H}$ couplings, indicating that both the resultant bridging phosphinidene-moiety and the phosphine/phosphite are *cis* to this hydride. The structural data of related clusters as well as the previously mentioned NMR data suggest that both **4a** and **b** have the structure shown in Scheme II. This was confirmed by the determination of the molecular structure of **4b** which is shown in Figure 2.

The structure of $[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)]$ (**4b**) is similar to that of $[Os_6(\mu\text{-}H)_2(CO)_{20}(NCMe)(\mu\text{-}PH)]$[9] in that the planes of the two phosphinidene-



1 **3a, b** **4a, b**

SCHEME II Formation of $[Os_6(\mu\text{-}H)_2(CO)_{20}\{PR_3\}(\mu_3\text{-}PH)]$ (R = Ph, **4a**; R = OMe, **4b**).

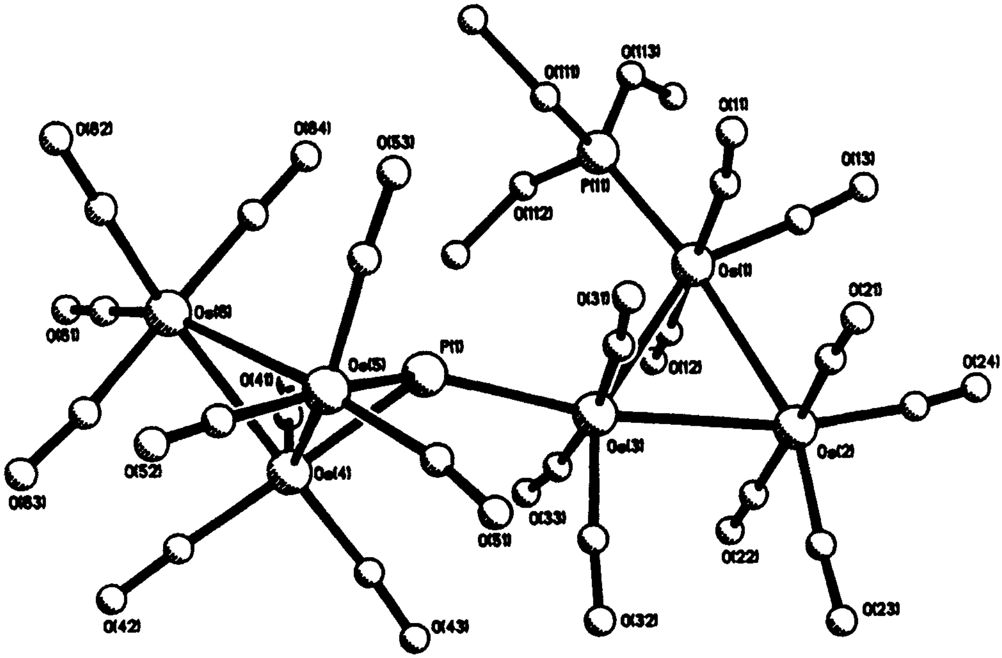


FIGURE 2 Molecular structure of $[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)]$ (**4b**) showing the atom numbering scheme.

linked trinuclear clusters are approximately perpendicular to each other; the dihedral angle in the structure of [$Os_6(\mu\text{-}H)_2(CO)_{20}(NCMe)(\mu\text{-}PH)$] is 89.8°, that of the structure of **4b** is 88.6°. This orientation of the two triangles is probably a result of steric hindrance. The bridging phosphinidene moiety brings the two clusters in close contact and the carbonyl ligands of the two clusters are virtually interlocked, as can be seen from the space-filling diagram of Figure 3. A rotation around the Os(3)—P(1)-bond would cause increased steric interaction between the equatorial carbonyls of Os(4), Os(5) and the carbonyls of Os(3). The fixed structure of **4b** and the previously mentioned strong similarity of the ^1H and ^{31}P NMR spectra of **4a** and **b** indicate that **4a** and **b** are isostructural. There is no evidence of *endo*-isomers. Although the formation of such isomers are, in theory, possible, it is expected that these isomers will be sterically unfavourable and the formation of the *exo*-isomers are therefore strongly favoured.

Whereas the reactivity of **1** has been explored for cluster build-up, this is not the case for its ruthenium analogue [$Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)$] (**5**). Therefore, **5** was reacted with [$Os_3(CO)_{11}(NCMe)$] under conditions similar to those used for the synthesis of **4a** and **b**. Purification by thin layer chromatography afforded the 'semi-interstitial' phosphido-cluster [$Ru_3Os_3(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}P)$] (**6**) in moderate yield. This cluster has been characterized by IR, ^1H and ^{31}P NMR spectroscopy as well as mass spectroscopy. The spectroscopic data are entirely consistent with the proposed structure, which is based on the similarity of the IR spectrum of this cluster with that of [$Os_6(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}As)$],[14] whose structure has been determined by single crystal X-ray crystallography. The large downfield shift observed in the ^{31}P NMR spectrum of **6** indicates that the phosphorus atom is coordinated to several metal atoms.

There are two possible pathways by which **6** could be formed (Scheme III). The first one involves the formation of the phosphinidene-cluster [$Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PH)$] which subsequently reacts with [$Os_3(CO)_{11}(NCMe)$] ("$Os_3(CO)_{11}$") by oxidative addition of the remaining P—H bond to form **6**. Alternatively, the phosphinidene-bridged cluster [$Ru_3Os_3(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)$] is initially formed, after

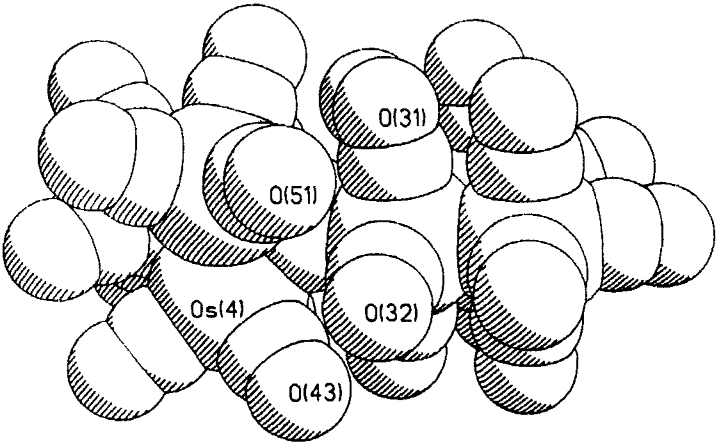
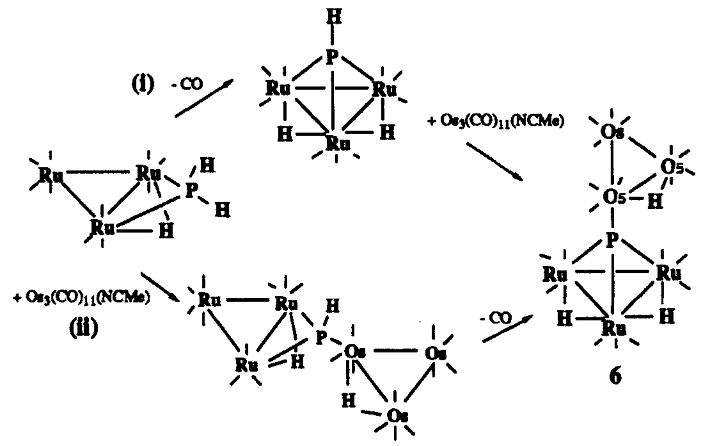


FIGURE 3 Space-filling diagram of [$Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)$] (**4b**).



SCHEME III Possible pathways for the formation of $[Ru_3Os_3(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}P)]$ (**6**).

which one carbonyl is ejected from the ruthenium triangle and oxidative addition of the P—H bond forms the 'semi-interstitial' phosphido-cluster. It is possible that both reaction pathways are followed. Some circumstantial evidence supports the second pathway: (i) the homometallic species $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$, analogous to the postulated intermediate $[Ru_3Os_3(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$, is already known; (ii) the osmium-acetonitrile bond may be expected to be more labile than the ruthenium-carbonyl bond, and (iii) attempts to form the cluster $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PH)]$ have so far proven unsuccessful. Attempts to further metallate the phosphorus atom of **6** by thermolysis or UV irradiation only resulted in decomposition of the cluster.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were distilled over the appropriate drying agents prior to use. Infra-red spectra were recorded as solutions in 0.5 mm NaCl cells on a Perkin Elmer 983 grating spectrometer or Perkin-Elmer 1710 Fourier-transform spectrometer with carbon monoxide as calibrant. Mass spectra were obtained on Kratos MS50, MS902 or MS890 spectrometers. Proton and phosphorus NMR spectra were recorded on Bruker WM250 or AM400 spectrometers. Routine separation of products was performed by thin-layer chromatography using commercially prepared glass plates, pre-coated to 0.25 mm thickness with Merck Kieselgel $60F_{254}$ or 2 mm thick plates prepared in the University of Cambridge Chemical Laboratory. The starting material $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**1**) was synthesized according to literature methods.[9,12]

Synthesis of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH(CH_2)_6I))]$ (**2a**): In a typical reaction, 3 drops $I(CH_2)_6I$ (0.5 mmol, excess) were added to 41 mg (0.046 mmol) of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ and 68 mg ($\approx$0.4 mmol, excess) BaO in 5 ml MeCN and the reaction was stirred at room temperature until no $\nu_{C—O}$ resonances due to the starting material could be detected (approx. 2 hrs). Ensuing purification by TLC (hexane/CH_2Cl_2 1:1 v/v) yielded yellow $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}P((CH_2)_6I)H)]$ (**2a**) in 8% yield.

Synthesis of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH(CH_2)_{10}I))]$ (**2b**): In a typical reaction, 2 drops $I(CH_2)_{10}I$ (0.5–0.9 mmol, excess) were added to 21 mg (0.024 mmol) of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ and 116 mg ($\approx$0.8 mmol, excess) BaO in 5 ml MeCN and the reaction was stirred at room temperature until no $\nu_{C—O}$ resonances due to the starting material could be detected (approx. 2 hrs). Ensuing purification by TLC (hexane/CH_2Cl_2 1:1 v/v) yielded yellow $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}P((CH_2)_{10}I)H)]$ (**2b**) in 11% yield.

Synthesis of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH(C_4H_8OH))]$ (**2c**): In a typical reaction, a solution of 40 mg (0.045 mmol) of **1** and an excess of 1-butane-epoxide (20 drops) in acetonitrile was stirred at elevated temperature (70°C) until no ν_{C-O} resonances due to the starting material could be detected (approx. 24 hrs). The solution was filtered through a silica plug using dichloromethane containing 1% trifluoroacetic acid as eluant. Thin layer chromatography (hexane/CH_2Cl_2, 1:1 v/v) resulted in the formation of 7 mg (0.007 mmol, 15%) of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH(C_4H_8OH))]$ (**2c**).

Synthesis of $[Os_3(CO)_{10}(PPh_3)(NCMe)]$ (**3a**): In a typical reaction, a total of 12.5 mg (0.167 mmol) of freshly sublimed trimethylamine oxide was dissolved in 25 ml of a 1:1 dichloromethane/acetonitrile-mixture and this solution was added dropwise over a period of twelve hours to a solution of 164.2 mg of $[Os_3(CO)_{11}(PPh_3)]$ in *ca.* 50 ml of a 1:1 dichloromethane/acetonitrile solution. Infra-red spectroscopy indicated complete conversion to $[Os_3(CO)_{10}(PPh_3)(NCMe)]$. The solution was reduced in volume and subjected to thin layer chromatography using a 3:2 hexane/dichloromethane mixture as eluant. Three bands were isolated; they were, in order of decreasing R_f: $[Os_3(CO)_{11}(PPh_3)]$, yellow, *ca.* 10 mg; $[Os_3(CO)_{10}(PPh_3)_2]$, orange-yellow, *ca.* 5 mg and $[Os_3(CO)_{10}(PPh_3)(NCMe)]$ (**3a**), orange-yellow, 77.5 mg (0.067 mmol, 47%).

Synthesis of $[Os_3(CO)_{10}\{P(OMe)_3\}(NCMe)]$ (**3b**): In a typical reaction, 86.3 mg (0.086 mmol) of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ was dissolved in 100 ml of a 2:1 dichloromethane/acetonitrile mixture. A total of 7.0 mg Me_3NO (0.093 mmol, ≈1.1 eq.) was dissolved in *ca.* 10 ml of a 1:1 dichloromethane/acetonitrile mixture. This solution was added dropwise to the solution of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ over a period of approximately nine hours. I.r. spectroscopy indicated complete conversion to $[Os_3(CO)_{10}\{P(OMe)_3\}(NCMe)]$. The reaction was stopped and the solution concentrated in volume to *ca.* 5 ml, after which it was subjected to thin layer chromatography. Three yellow bands were found. They were, in order of decreasing R_f: $[Os_3(CO)_{11}\{P(OMe)_3\}]$, yellow, 5 mg (0.005 mmol, 6%); $[Os_3(CO)_{10}\{P(OMe)_3\}_2]$, yellow (trace) and $[Os_3(CO)_{10}\{P(OMe)_3\}(NCMe)]$ (**3b**), *ca.* 80 mg (0.078 mmol, 90%). Yields quoted are after recrystallization from dichloromethane/hexane.

Synthesis of $[Os_6(\mu\text{-}H)_2(CO)_{20}PPh_3(\mu_3\text{-}PH)]$ (**4a**): In a typical reaction, a total of *ca.* 25 mg (0.022 mmol) of **3a** and 22 mg (0.024 mmol) of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**1**) were dissolved in *ca.* 40 ml of toluene and stirred at 45°C for 24 hours. After the reaction had been stopped, the solvent was removed under a stream of nitrogen. The product(s) were redissolved in a small amount of dichloromethane and subjected to t.l.c. using a 1:1 mixture of dichloromethane/hexane as eluant. Four yellow bands were observed. They were, in order of decreasing R_f: $[Os_3(CO)_{11}(PPh_3)]$, (trace); $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$, yellow, 2 mg; $[Os_6(\mu\text{-}H)_2(CO)_{20}(PPh_3)(\mu_3\text{-}PH)]$ (**4a**), 20 mg (0.010 mmol, 45%); and a fourth band (trace), not isolated. Yields quoted are after recrystallization from dichloromethane/hexane.

Synthesis of $[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)]$ (**4b**): A total of 66 mg (0.065 mmol) of **3b** and 57 mg (0.064 mmol) of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**1**) were dissolved in *ca.* 75 ml of toluene and stirred at 45°C for 24 hours. (Initially, the compounds did not dissolve completely, but did so as the solvent was heated.) After the reaction had been stopped, the solvent was removed under a stream of nitrogen. The product(s) were redissolved in a small amount of dichloromethane and subjected to t.l.c. using a 1:1 mixture of dichloromethane/hexane as eluant. Four yellow bands were observed. They were, in order of decreasing R_f: $[Os_3(CO)_{11}\{P(OMe)_3\}]$, 4 mg (0.004 mmol, 6%); $[Os_3(CO)_{10}\{P(OMe)_3\}(NCMe)]$/ $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$; $[Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)]$ (**4b**), 88.2 mg (0.046 mmol, 73%); and a fourth band (trace), not isolated. Yields quoted are after recrystallization from dichloromethane/hexane.

Synthesis of $[Ru_3Os_3(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}P)]$ (**6**): In typical reactions, $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**5**) was reacted with $[Os_3(CO)_{11}(NCMe)]$ in either toluene at 50°C or dichloromethane at room temperature for periods of 14–24 h. Purification by thin layer chromatography (CH_2Cl_2/hexane, 1:1 v/v) afforded $[Ru_3Os_3(\mu\text{-}H)_3(CO)_{20}(\mu_4\text{-}P)]$ (**6**) in 7–29% yield.

X-Ray Crystal Structure Determination of **4b**

Suitable crystals of **4b** were grown by slow evaporation of dichloromethane/hexane solution, and a single crystal glued to a glass fibre with epoxy resin and transferred to a Nicolet R3mV diffractometer.

Crystal data: $C_{23}H_{12}O_{23}P_2Os_6$, M = 1859.65, monoclinic, space group $P2_1/c$ (No. 14), a = 13.699(12), b = 16.09(3), c = 18.50(3), b = 104.78(9)°, V = 3943(10) Å^3 (by least-squares refinement of diffractometer angles from 25 automatically centered reflections in the range 20 < 2θ < 25°, l = 0.71069 Å), Z = 4, D_c = 3.132 g cm^{-3}, F(000) = 3280. Yellow block. Crystal dimensions 0.22 × 0.24 × 0.35 mm, μ(Mo-K_α) = 193.45 cm^{-1}

TABLE II

Fractional atomic coordinates (× 10^4) for
[$Os_6(\mu\text{-}H)_2(CO)_{20}\{P(OMe)_3\}(\mu_3\text{-}PH)$] (**4b**)

	x	y	z
Os(1)	1660(1)	8188(1)	1206(1)
Os(2)	3386(1)	8991(1)	2143(1)
Os(3)	1529(1)	9192(1)	2538(1)
Os(4)	-753(1)	9061(1)	3726(1)
Os(5)	-966(1)	10567(1)	2905(1)
Os(6)	-2674(1)	9537(1)	2818(1)
P(1)	-180(8)	9332(7)	2654(7)
P(11)	198(9)	7576(7)	604(7)
O(111)	-654(24)	8258(18)	345(18)
C(12)	1989(34)	7259(17)	1807(21)
O(33)	1610(22)	7629(12)	3439(15)
C(31)	1198(26)	10123(13)	1939(16)
O(24)	4926(22)	8341(19)	1398(18)
O(12)	2136(24)	6619(10)	2104(17)
O(112)	-245(30)	6916(21)	1060(20)
C(21)	3074(30)	9915(10)	1532(12)
C(32)	2126(27)	9782(12)	3396(10)
C(22)	3622(25)	8117(13)	2815(14)
C(11)	1345(35)	9070(18)	545(20)
O(23)	4632(20)	10066(19)	3366(14)
C(33)	1654(39)	8229(17)	3101(24)
O(22)	3765(23)	7542(12)	3206(15)
O(113)	72(29)	7044(26)	-106(22)
O(52)	-2044(25)	11931(16)	3499(23)
O(13)	2861(25)	7591(20)	154(16)
O(41)	-1212(32)	7291(10)	3230(28)
O(31)	932(24)	10703(15)	1568(18)
O(43)	1341(13)	8797(23)	4705(18)
O(32)	2592(25)	10109(18)	3935(10)
O(11)	1033(28)	9649(15)	187(20)
O(21)	2926(25)	10519(14)	1178(18)
C(61)	-3277(34)	8572(17)	3035(28)
C(51)	233(15)	11152(21)	3070(22)
C(52)	-1668(30)	11379(20)	3270(24)
O(51)	897(20)	11620(18)	3242(20)
C(23)	4122(17)	9662(20)	2900(15)
C(24)	4394(23)	8688(25)	1693(23)
O(63)	-2946(26)	10420(20)	4188(12)
O(61)	-3662(29)	7971(17)	3172(27)
C(63)	-2781(39)	10122(15)	3657(10)
C(13)	2420(34)	7802(30)	581(24)
C(111)	-1753(46)	7988(35)	-59(35)
O(53)	-1581(43)	11051(30)	1281(7)
C(53)	-1368(30)	10875(30)	1910(7)
C(41)	-1057(29)	7976(10)	3421(27)
C(43)	538(14)	8857(28)	4307(23)
C(112)	-462(44)	6990(35)	1780(33)
C(113)	677(54)	6315(43)	-89(39)
O(42)	-1541(27)	9065(21)	5104(12)
C(42)	-1265(38)	9081(17)	4560(18)
O(62)	-4414(17)	10475(19)	1835(18)
C(62)	-3730(22)	10131(18)	2216(25)
C(64)	-2522(37)	9063(34)	1943(15)
O(64)	-2407(33)	8760(27)	1401(13)

TABLE III

Selected bond lengths (Å) and bond angles (o) for $[Os_6(\mu\text{-}H)_2(CO)_{20}\cdot\{P(OMe)_3\}(\mu_3\text{-}PH)]$ (**4b**)

Os(1)-Os(2)	2.858 (5)
Os(1)-Os(3)	2.989 (6)
Os(1)-P(11)	2.256 (12)
Os(2)-Os(3)	2.838 (6)
Os(3)-P(1)	2.416 (13)
Os(4)-Os(5)	2.834 (6)
Os(4)-Os(6)	2.842 (6)
Os(4)-P(1)	2.352 (14)
Os(5)-Os(6)	2.839 (6)
Os(5)-P(1)	2.361 (12)

Os(2)-Os(1)-Os(3)	58.0(1)
Os(2)-Os(1)-P(11)	171.8(4)
Os(3)-Os(1)-P(11)	114.2(4)
P(11)-Os(1)-C(12)	89.6(12)
P(11)-Os(1)-C(11)	88.9(13)
P(11)-Os(1)-C(13)	96.6(14)
Os(1)-Os(2)-Os(3)	63.3(1)
Os(1)-Os(3)-Os(2)	58.7(1)
Os(1)-Os(3)-P(1)	112.8(3)
Os(2)-Os(3)-P(1)	170.5(3)
P(1)-Os(3)-C(31)	83.2(12)
P(1)-Os(3)-C(32)	95.8(12)
P(1)-Os(3)-C(33)	88.9(17)
Os(5)-Os(4)-Os(6)	60.0(1)
Os(5)-Os(4)-P(1)	53.2(3)
Os(6)-Os(4)-P(1)	84.8(3)
P(1)-Os(4)-C(41)	90.9(16)
P(1)-Os(4)-C(43)	92.7(13)
P(1)-Os(4)-C(42)	168.1(9)
Os(4)-Os(5)-Os(6)	60.1(1)
Os(4)-Os(5)-P(1)	52.9(3)
Os(6)-Os(5)-P(1)	84.7(3)
P(1)-Os(5)-C(51)	91.8(10)
P(1)-Os(5)-C(52)	166.4(13)
P(1)-Os(5)-C(53)	93.7(14)
Os(4)-Os(6)-Os(5)	59.9(1)
Os(3)-P(1)-Os(4)	126.7(5)
Os(3)-P(1)-Os(5)	126.7(5)
Os(4)-P(1)-Os(5)	73.9(4)

Data collection and processing: Nicolet R3mV diffractometer, 5818 reflections were measured in the range $5.0 < 2q < 45.0°$ ($\pm h$, $+k$, $\pm l$) using a $w/2\theta$ scan mode and graphite monochromated Mo-K_α radiation. 5155 unique reflections [$R_{int} = 0.028$ after a semi-empirical absorption correction (max., min. transmission factors 0.016, 0.003)], giving 3413 observed reflections with $F > 6\sigma(F)$. Three check reflections showed no significant variations during data collection.

Structure analysis and refinement: The structure was solved by direct methods (Os atoms) and Fourier difference techniques and refined by full-matrix least-squares Os, P and carbonyl O atoms anisotropic. H-atoms were not included, and constraints were applied to the Os—C(carbonyl) and C—O distances (Os—C 1.850(1), C—O 1.160(1)). The weighting scheme $w^{-1} = \sigma^2(F) + 0.0080F^2$ was introduced. The converged residuals for 362 parameters were $R = 0.091$ and $R_w = 0.095$. The structure was solved and refined using SHELXTL PLUS[15] on a Micro Vax II computer. Fractional atomic coordinates are listed in Table II. Selected bond lengths and bond angles are listed in Table III. Full listings of bond parameters and displacement parameters may be obtained from the Cambridge Crystallographic Data Centre.

ACKNOWLEDGEMENTS

We wish to thank SERC for financial support and Johnson Matthey plc for generous loans of ruthenium and osmium compounds. We also wish to thank Dr. S. Hietkamp (CSIR, South Africa) for a gift of $[Os_3(CO)_{12}]$. E. N. wishes to thank the Cambridge Philosophical Society and the Adolf Lindgren Foundation for financial support and King's College, Cambridge, for the award of an External Research Studentship.

REFERENCES AND NOTES

1. Present address: Bayer AG, Werk Ürdingen, Business Unit Organic Chemicals, Building R-79, D-47812 Krefeld, Federal Republic of Germany.
2. Present address: Inorganic Chemistry 1, Chemical Center, Lund University, Box 124, S-221 00 Lund, Sweden.
3. W. L. Gladfelter and K. J. Roesselet, in "The Chemistry of Metal Cluster Complexes," D. F. Shriver, H. D. Kaesz and R. D. Adams, eds., VCH Publishers, Weinheim, 1990.
4. D. J. Darensbourg, in "Metal-Metal Bonds and Clusters in Chemistry and Catalysis," J. P. Fackler, ed., Plenum, New York, N.Y., 1990.
5. K. Whitmire, *J. Coord. Chem.*, **17,** 95 (1988).
6. G. Huttner and K. Knoll, *Angew. Chem. Int. Ed. Engl.*, **26,** 743 (1987).
7. J. L. Vidal, W. E. Walker and R. C. Schoening, *Inorg. Chem.*, **20,** 238 (1981).
8. H. Vahrenkamp, *Struct. Bonding (Berlin)*, **32,** 1 (1977).
9. S. B. Colbran, F. J. Lahoz, P. R. Raithby, J. Lewis, B. F. G. Johnson and C. J. Cardin, *J. Chem. Soc. Dalton Trans.*, 173 (1988).
10. S. B. Colbran, B. F. G. Johnson, J. Lewis and R. M. Sorrell, *J. Chem. Soc. Chem. Comm.*, 525 (1986).
11. S. B. Colbran, B. F. G. Johnson, J. Lewis and R. M. Sorrell, *J. Organomet. Chem.*, **296,** C1 (1985).
12. L. Heuer, B. F. G. Johnson, J. Lewis and C. N. Kenney, *Polyhedron*, **10,** 1955 (1991).
13. (a) F. Iwasaki, M. J. Mays, P. R. Raithby, P. L. Taylor and P. J. Wheatley, *J. Organomet. Chem.*, **213,** 185 (1981); (b) P. L. Taylor, Ph.D. thesis, University of Cambridge, 1982.
14. K. Guldner, B. F. G. Johnson, J. Lewis, A. D. Massey and S. Bott, *J. Organomet. Chem.*, **408,** C 13 (1991).
15. SHELXTL PLUS, Version 3.4, Nicolet Instruments Corporation, Madison, WI, 1988.