= 2.47 Å, d(Hg,Cl) = 2.48 Å, d(P,H) = 1.40 Å, and θ(P,Hg,P) = θ(Cl,Hg,Cl) = θ(H,P,H) = 110°. All further calculations on geometrically distorted molecules (θ(P,Hg,P) and θ(Cl,Hg,Cl) being the only distorted structural parameters) were performed without further changes of the H_{ii}'s.

Coupling constants J(Hg,P) were calculated by using the formalism of Pople and Santry.[33]

$$J(\mathrm{A,B}) = {}^{32}/_{9}h\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}|\Psi_{s,\mathrm{A}}(0)|^2|\Psi_{s,\mathrm{B}}(0)|^2\pi_{\mathrm{AB}}$$

$$\pi_{\mathrm{AB}} = +4\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}}({}^3\Delta E_{ij})^{-1}C^{s}_{i,\mathrm{A}}C^{s}_{j,\mathrm{A}}C^{s}_{i,\mathrm{B}}C^{s}_{j,\mathrm{B}}$$

$|\Psi_{s,\mathrm{M}}(0)|^2$ is the s density of the valence s orbital centered on A or B, γ is a gyromagnetic ratio, ${}^3\Delta E_{ij}$ are triplet excitation energies, and $C^{s}_{i,\mathrm{A}}$ ($C^{s}_{j,\mathrm{A}}$, etc.) is the coefficient of an atomic s orbital centered on A (or B) in the ith MO (jth MO). The coefficients were produced by the EHMO calculations, ${}^3\Delta E_{ij}$ was taken as the difference between the eigenvalues E_i and E_j, and the s density at the nucleus was that of the neutral atom for phosphorus and that of $d^9s^1p^1$ mercury(I).

Multiple Linear Regression. The data in Table II were used with unit weight to determine the coefficients a', b, and c in the expression J(Hg,P) = a' + b[θ(P,Hg,P) - θ^0(P,Hg,P)] + c[θ(X,Hg,X) - θ^0(X,Hg,X)], where θ^0(P,Hg,P) = $\sum\theta$(P,Hg,P)/N and θ^0(X,Hg,X) = $\sum\theta$(X,Hg,X)/N, with N the number of observations. Choosing the origin of the regression at θ^0, the "center of mass", minimizes the trace of the variance–covariance matrix. Results are (σ in parentheses) a' = 4149 (117) Hz, b = 25.1 (5.5) Hz/deg, c = -48.7 (8.3) Hz/deg, r^2 = 0.93, and $(\sum\Delta^2/N-3))^{1/2}$ = 350 Hz (standard deviation of an observation of unit weight; $\Delta = J_{\mathrm{obsd}} - J_{\mathrm{calcd}}$); elements of the correlation matrix are $C(a',b)$ = 0, and $C(b,c)$ = 0.3. Results for θ^0(P,Hg,P) = θ^0(X,Hg,X) = 109.5° are a'' = 3271 (155) Hz, $C(a'',b)$ = -0.47, and $C(a'',c)$ = 0.31, and all others are the same as above. The values given in the Discussion are obtainable from the above results.

Acknowledgment. R.W.K. and M.P. thank the Schweizerischen Nationalfonds zur Förderung der Wissenschaftlichen Forschung for financial support and Mr. L. Zoller for computational assistance.

Registry No. I, 27902-66-5; II, 14057-00-2; III, 80063-20-3; $Hg(ac)_2$(*cis*-$Ph_2PCH{=}CHPPh_2$), 80063-21-4; $HgCl_2$(*cis*-$Ph_2PCH{=}CHPPh_2$), 80063-22-5; $Hg(SCN)_2$(*cis*-$Ph_2PCH{=}CHPPh_2$), 80106-35-0; $Hg(CN)_2$(*cis*-$Ph_2PCH{=}CHPPh_2$), 80083-22-3; $Hg((EtO)_2PO_2)_2$(*cis*-$Ph_2PCH{=}CHPPh_2$), 80083-23-4; HgI_2(*cis*-$Ph_2PCH{=}CHPPh_2$), 80083-24-5; $Hg(ac)_2(PPh_3)_2$, 66119-73-1; $HgCl_2(PPh_3)_2$, 14494-85-0; $HgBr_2(PPh_3)_2$, 14586-76-6; $Hg(SCN)_2(PPh_3)_2$, 27290-69-3; $HgI_2(PPh_3)_2$, 14494-95-2.

Supplementary Material Available: Listings of structure factor amplitudes and of anisotropic thermal parameters (51 pages). Ordering information is given on any current masthead page.

(33) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).
(34) E. C. Alyea, S. A. Dias, G. Ferguson, and M. A. Khan, *J. Chem. Res., Synop.*, 360 (1979); *J. Chem. Res., Miniprint*, 4101 (1979).
(35) We are aware of the structure of $[Hg(ClO_4)_2(P(C_6H_{11})_3)_2]$,[34] with θ(P,Hg,P) = 170.7°, θ(O,Hg,O) = 137.9°, a calculated J(Hg,P) of 3400 Hg, and an observed J(Hg,P) of 3755 Hz. For calculation of J(Hg,P) we assume that we may consider this structure a case of four-coordinate Hg^{2+}. Note, however, that the Hg–O distances are 2.93 and 3.08 Å and that there are two further perchlorate oxygens O′ at 3.27 and 3.23 Å with an angle θ(O′,Hg,O′) = 141.3° and angles θ(O,Hg,O′) ≈ 40°. Thus an alternative interpretation of this structure would be in terms of a distorted octahedron.
(36) R. W. Kunz, Dissertation, ETH 6456, Zürich, 1979. Some of the coupling constants have been reported in the literature. Here we quote our own values, which are somewhat larger because they have been obtained at lower temperatures.

Notes

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Controlling the Number of Metal Sites to Which $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$ Coordinates in Tungsten Carbonyls[1]

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Received May 6, 1981

Polydentate phosphorus ligands have been used extensively in coordination chemistry for the past 20 years but in a narrowly focused manner that places principal emphasis on their chelating properties. A rich and relatively unexplored aspect of these ligands is their ability to bind in many arrangements other than the familiar fully chelated mode in monometallic species. This area of chemistry has been largely ignored because selective syntheses that eliminate tedious separations have not been available. In this work we have chosen to prepare complexes of $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$, triphos, to illustrate the utility of vinyl-addition reactions in controlling ligand coordination.

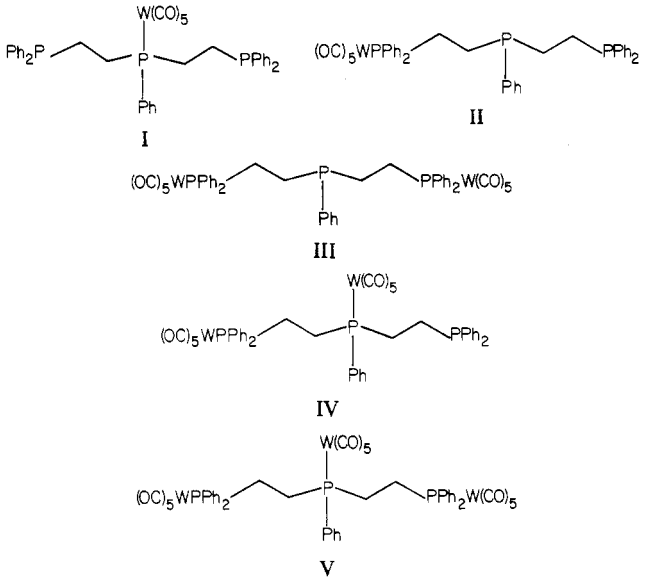
triphos was first synthesized in 1962.[3] Interest in the ligand lagged through the 1960s because its preparation was not attractive. It became widely used, however, following the discovery of high-yield syntheses by King,[4] Issleib,[5] and Meek.[6] At present it is routinely used in complexation studies such as those aimed at elucidating the reactions in homogeneous hydroformylation,[7] Fischer–Tropsch synthesis,[8] and catalytic hydrogenation.[9]

The ligating possibilities of triphos have been previously outlined, and specific examples of these species have been identified.[10] In order to synthesize such complexes routinely, however, it is necessary to find a method of controlling the number of metal sites to which the polyphosphine coordinates. Substitution reactions are in general inadequate because they too often lead to mixtures of isomers or mixtures of mono- and bimetallic products that may not be easily separated. In this work we report a method of obtaining the desired products that is based upon building the complex of interest from judiciously selected coordinated fragments. The approach has been used previously in the preparation of monodentate complexes of diphos, $Ph_2PCH_2CH_2PPh_2$, such as $(OC)_5M$(diphos) and $(OC)_4M(diphos)_2$ (M = Cr, Mo, W).[11]

(1) Presented at the 1980 Biennial Inorganic Chemistry Symposium at Guelph, Canada.
(2) (a) Eastern Illinois University. (b) Presently at Nicolet Technology Corp., Mt. View, CA 94041.
(3) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).
(4) R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, **93**, 4158 (1971).
(5) K. Issleib and H. Weichmann, *Z. Chem.*, **11**, 188 (1971).
(6) J. C. Cloyd, Jr., and D. W. Meek, *Inorg. Chim. Acta*, **6**, 607 (1972).
(7) K. Murata and A. Matsudo, *Bull. Chem. Soc. Jpn.*, **53**, 214 (1980); C. U. Pittman, Jr., W. D. Honnick, and J. J. Yang, *J. Org. Chem.*, **45**, 684 (1980); A. R. Sanger, *J. Mol. Catal.*, **3**, 221 (1978).
(8) G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **18**, 77 (1979).
(9) D. W. Meek, J. Niewahner, and P. Kreter, 1980 Biennial Inorganic Chemistry Symposium, Guelph, Canada; D. L. Dubois and D. W. Meek, *Inorg. Chim. Acta*, **19**, L29 (1979).
(10) R. B. King, *Acc. Chem. Res.*, **5**, 177 (1972).
(11) (a) R. L. Keiter, Y. Y. Sun, J. W. Brodack, and L. W. Cary, *J. Am. Chem. Soc.*, **101**, 2638 (1979). (b) Band assignment discussions are found in P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, 1975.

0020-1669/82/1321-1256$01.25/0

Chart I



There are five possible nonchelated triphos complexes of pentacarbonyltungsten (I–V, Chart I). This report outlines the syntheses of these five complexes and demonstrates the versatility of addition reactions in the selective coordination of polyphosphines.

Experimental Section

Physical Measurements. ^{31}P NMR and infrared spectra were obtained from chloroform solutions as described elsewhere.[11] Chemical shifts are reported with positive values downfield from the 85% phosphoric acid reference.

Materials. Diphenylvinylphosphine, phenyldivinylphosphine, diphenylphosphine, phenylphosphine, and tungsten hexacarbonyl were purchased from Pressure Chemical Co. and used without further purification. All reactions were carried out under a nitrogen atmosphere.

Preparations. The complexes $(OC)_5WPPh_2CH{=}CH_2$ and $(OC)_5WPPh_2H$ were prepared as described previously.[11] $(OC)_5WPPh(CH{=}CH_2)_2$ (86%) was prepared by THF displacement from $(OC)_5W(THF)$[12] and purified by molecular distillation (60 °C at 0.02 torr for 2 days).

$(OC)_5WPPh(CH{=}CH_2)_2$: IR 1983 (w) (B_1), 2075 (s) ($A_1^{(2)}$), 1941 (vs) (E + $A_1^{(1)}$) cm^{-1}; ^{31}P NMR δ 2.27 (J_{WP} = 236.3 Hz).

Anal. Calcd for $C_{15}H_{11}O_5PW$: C, 37.07; H, 2.28; P, 6.37. Found: C, 36.91; H, 2.44; P, 6.46.

$(OC)_5WPPh(CH_2CH_2PPh_2)_2$ (I). To $(OC)_5WPPh(CH{=}CH_2)_2$ (1.0 g, 2.1 mmol) and 2,2′-azobis(isobutyronitrile) (AIBN) (0.1 g) was added PPh_2H (0.75 mL). The mixture was heated for 24 h at 75 °C. Excess phosphine was removed by high vacuum. The oily mass eventually crystallized from CH_2Cl_2/CH_3OH (40%): mp 69–74 °C; IR 1983 (w) (B_1), 2074 (s) ($A_1^{(2)}$), 1940 (vs) (E + $A_1^{(1)}$) cm^{-1}.

Anal. Calcd for $C_{39}H_{33}P_3O_5W$: C, 54.56; H, 3.87; P, 10.82. Found: C, 54.40; H, 3.80; P, 10.99.

$(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2$ (II). A mixture of $(OC)_5WPhP(CH{=}CH_2)_2$ (1.2 mmol), PPh_2H (1.0 mmol), and AIBN (0.1 g) was heated for 24 h at 75 °C. Excess $PhP(CH{=}CH_2)_2$ was removed under high vacuum after which $(OC)_5WPPh_2H$ (1.0 mmol) and AIBN (0.1 g) were added. The new mixture was heated for 24 h at 75 °C. The oil that resulted was dissolved in a minimum of CH_2Cl_2 and an equal volume of CH_3OH. Refrigeration at 6 °C led to oil formation. The process was repeated twice more to give an oil, which was identified by ^{31}P NMR (20%): IR 1982 (w) (B_1), 2074 (s) ($A_1^{(2)}$), 1941 (vs) (E + $A_1^{(1)}$) cm^{-1}.

$PhP[CH_2CH_2PPh_2W(CO)_5]_2$ (III). To $(OC)_5WPPh_2(CH{=}CH_2)$ (2.0 g, 3.7 mmol) and AIBN (0.1 g) was added $PPhH_2$ (3.7 mmol). The mixture was heated for 24 h at 75 °C. Unreacted $PPhH_2$ was removed by high vacuum. Attempts to crystallize the product from CH_3OH/CH_2Cl_2 gave an oil, which was chromatographed (silica gel) with 80% petroleum ether/20% ethyl acetate. An oil was obtained which crystallized after a period of 2 months (58%): mp 80–85 °C; IR 1983 (w) (B_1), 2074 (s) ($A_1^{(2)}$, 1941 (vs) (E + $A_1^{(1)}$) cm^{-1}.

Anal. Calcd for $C_{44}H_{33}P_3W_2O_{10}$: C, 44.68; H, 2.79; P, 7.86. Found: C, 44.81; H, 2.78; P, 7.56.

$(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2)$. To a mixture of $(OC)_5WPPh(CH{=}CH_2)_2$ (2.67 g, 5.45 mmol) and KO(*t*-Bu) (0.1 g) in THF (150 mL) was added dropwise $(OC)_5WPPh_2H$ (1.31 g, 2.57 mmol) dissolved in THF (50 mL) over a 1-h period. The residue, obtained after solvent removal, was crystallized from CH_2Cl_2/CH_3OH (56%). The first fraction was contaminated with the trimetallic complex (V): mp 123–125 °C; IR 1983 (w) (B_1), 2074 (s) ($A_1^{(2)}$), 1941 (vs) ($A_1^{(1)}$ + E) cm^{-1}. Absorption bands are somewhat broadened because of inequivalent $W(CO)_5$ groups.

Anal. Calcd for $C_{32}H_{22}O_{10}W_2P_2$: C, 38.57; H, 2.21; P, 6.22. Found: C, 38.30; H, 2.09; P, 6.08.

$(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2$ (IV). To a mixture of $(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2)$ (1.16 g, 1.16 mmol) and KO(*t*-Bu) (0.1 g) in THF (150 mL) was added PPh_2H (1.12 mmol). The mixture was heated under reflux for 1.5 h, after which solvent and excess PPh_2H were removed to yield an oily mass. The product was crystallized from CH_2Cl_2/CH_3OH (40%): mp 139–141 °C; IR 1983 (w) (B_1), 2073 (s) ($A_1^{(2)}$), 1941 (vs) ($A_1^{(1)}$ + E) cm^{-1}.

Anal. Calcd for $C_{44}H_{33}P_3W_2O_{10}$: C, 44.68; H, 2.79; P, 7.86. Found: C, 44.61; H, 2.80; P, 8.11.

$(OC)_5WPPh[CH_2CH_2PPh_2W(CO)_5]_2$ (V). To a mixture of $(OC)_5WPPh_2H$ (2.12 g, 4.15 mmol) and KO(*t*-Bu) (0.2 g) in THF (25 mL) was added (over a 1-h period) $(OC)_5WPPh(CH{=}CH_2)_2$ (1.03 g, 2.12 mmol) in THF (25 mL). The white product was crystallized from CH_2Cl_2/CH_3OH (79%): mp 160–162 °C; IR (signals broad) 1985 (w) (B_1), 2076 (s) ($A_1^{(2)}$), 1941 (vs) ($A_1^{(1)}$ + E) cm^{-1}.

Anal. Calcd for $C_{49}H_{33}O_{15}W_3P_3$: C, 39.07; H, 2.21; P, 6.17. Found: C, 38.92; H, 2.49; P, 5.92.

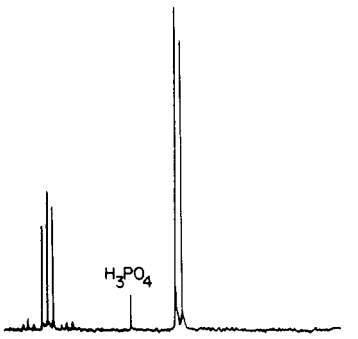


Figure 1. $^{31}P\{H\}$ NMR spectrum of $(OC)_5WPPh(CH_2CH_2PPh_2)_2$.

Results and Discussion

The complex $(OC)_5WPPh(CH{=}CH_2)_2$ is a nonviscous liquid, which can be obtained in high purity by molecular distillation. It is stable in air at room temperature and can be stored for long periods of time if it is protected from light. It is an excellent starting material for the production of I, undergoing free radical induced addition of diphenylphosphine.[13]

$$(OC)_5WPPh(CH{=}CH_2)_2 + 2PPh_2H \xrightarrow[75\ °C]{AIBN} Ph_2PCH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2$$
I

The structure of I is unambiguously established by its ^{31}P spectrum (Figure 1), which shows a downfield triplet (7.3 ppm) and an upfield doublet (−12.5 ppm) of appropriate intensities ($^3J_{PP}$ = 33.8 Hz). ^{183}W satellites are observed for the coordinated phosphorus atom (J_{WP} = 236.7 Hz). In solution, I is slowly oxidized to a monoxide which shows ^{31}P chemical

(12) W. Strohmeier and F. Müller, *Chem. Ber.*, **102**, 3608 (1969).

(13) D. W. Meek, D. L. Dubois, and J. Tiethof, *Adv. Chem. Ser.*, **No. 150**, 335 (1976). 2,2′-Azobis(isobutyronitrile), AIBN, is a convenient free radical source for these reactions just as it is for the syntheses of uncoordinated polyphosphines.

Table I. ^{31}P NMR Data of Pentacarbonyltungsten Complexes of $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$

complex	δ_{WPPh}	δ_{WPPh_2}	δ_{PPh}	δ_{PPh_2}	J_{PP}, Hz	J_{WP}, Hz
I	7.3			−12.5	33.8	236.7
II		12.5	−16.6	−12.8	29.4[a]	239.4
					31.1	
III		13.6	−17.3		30.7	239.9
IV	6.8	12.7		−12.1	36.5[b]	238.6[c]
					32.7	239.9[d]
V	7.5	13.5			34.7	239.4[c]
						242.0[d]
I (oxide)	7.4			−12.6	43.2[e]	[g]
				31.1[f]	34.2	
II (oxide)			40.7[f]			[g]
II (oxide)				32.7[f]		[g]
III (oxide)			45.6[f]		46.4[e]	[g]
IV (oxide)		12.4		29.6[f]	46.3[e]	[g]
					31.9	

[a] $J_{PPh_2W\text{-}PPh}$. [b] $J_{PPhW\text{-}PPh_2}$. [c] J_{PPhW}. [d] J_{PPh_2W}. [e] δ_{PPO}. [f] δ_{PO}. [g] Unresolved.

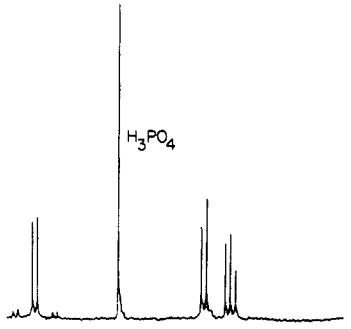


Figure 2. ^{31}P{H} NMR spectrum of $(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2$.

shifts at −12.6, 7.4, and 31.1 ppm for uncoordinated phosphorus, phosphorus coordinated to tungsten, and phosphorus coordinated to oxygen, respectively. Phosphorus–phosphorus coupling between coordinated phosphorus atoms is 43.2 Hz and between coordinated and uncoordinated atoms is 34.2 Hz (Table I).

Obtaining II, a structural isomer of I, was synthetically

$$PhP(CH{=}CH_2)_2 + PPh_2H \xrightarrow{AIBN} PhP(CH{=}CH_2)(CH_2CH_2PPh_2)$$

$$PhP(CH{=}CH_2)(CH_2CH_2PPh_2) + (OC)_5WPPh_2H \xrightarrow{AIBN} \underset{II}{(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2}$$

difficult and was best accomplished by a two-step reaction involving $Ph_2PCH_2CH_2PPh(CH{=}CH_2)$ as an unisolated intermediate. A downfield doublet (12.5 ppm, $^3J_{PP}$ = 29.4 Hz) flanked by ^{183}W satellites (J_{WP} = 239.4 Hz), an upfield doublet (−12.8 ppm, J_{PP} = 31.1 Hz), and a doublet of doublets (−16.6 ppm) (Figure 2) clearly identifies the complex and dramatically distinguishes it from isomer I. Isomer II is somewhat more air sensitive than isomer I, and mixtures of $(OC)_5WPPh_2CH_2CH_2PPh(O)CH_2CH_2PPh_2$ ($\delta_{P=O}$ 40.7) and $(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2PPh_2(O)$ ($\delta_{P=O}$ 32.7) were observed spectroscopically but not isolated.

Other reported examples of monoligated monometallic complexes are the unseparated isomers of $CH_3COFe(CO)(triphos)(\eta^5\text{-}C_5H_5)$ and of $(OC)_4Fe(triphos)$.[14,15] In addition, $[V(CO)_5(triphos)]^-$ has been observed in solution by IR and ^{51}V NMR spectroscopy.[16]

It one wishes to obtain pure monoligated monometallic isomers of triphos, clearly, substitution reactions are not desirable. Vinyl-addition reactions provide a route whereby the coordination of terminal or central phosphorus atoms is not left to chance. Thus it is possible to synthesize I without generating II and vice versa. In addition, the absence of vacant coordination sites during the course of the reaction precludes the formation of phosphine-bridged polymetallic species.

Complex III was also obtained by free radical addition. A

$$(OC)_5WPPh_2(CH{=}CH_2) + PPhH_2 \rightarrow \underset{III}{(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2W(CO)_5}$$

downfield doublet (13.6 ppm, $^3J_{PP}$ = 30.7 Hz) with ^{183}W satellites (J_{WP} = 239.9 Hz) and an upfield triplet (−17.3 ppm) establish the structure of III. Air oxidation of III gave the oxide, which revealed a downfield triplet (δ_{PO} 45.6, J_{PP} = 46.4 Hz), which was assigned to the phosphoryl group.

Complex IV, the isomer of III, was prepared in two steps.

$$(OC)_5WPPh(CH{=}CH_2)_2 + (OC)_5WPPh_2H \xrightarrow{KO(t\text{-}Bu)} (OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2)$$

$$(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH{=}CH_2) + PPh_2H \xrightarrow{KO(t\text{-}Bu)} \underset{IV}{(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5]CH_2CH_2PPh_2}$$

The intermediate was isolated as a white solid in reasonable yield (56%) (δ_{WPPh_2} 12.8, J_{PP} = 35.7 Hz, J_{WP} = 240.9 Hz; δ_{WPPh} 4.5, J_{WP} = 238.6 Hz) even though separation of it from starting materials and trimetallic complex, V, was required. Characterization of IV by ^{31}P NMR confirms its structural arrangement. The uncoordinated phosphorus atom gives rise to a doublet (−12.1 ppm, $^3J_{PP}$ = 36.5 Hz) as does the coordinated terminal phosphorus atom (δ = 12.7, J_{PP} = 32.7 Hz, J_{WP} = 239.9 Hz). The coordinated central phosphorus atom appears as a doublet of doublets (6.8 ppm, J_{WP} = 238.6 Hz). The oxide, occasionally found as a contaminant, gives rise to two doublets (δ_{WPPh_2} 12.4, J_{PP} = 31.9 Hz; δ_{PO} 29.6, J_{PP} = 46.3 Hz) and a doublet of doublets obscured by signals from its precursor. ^{183}W satellites were not observed because of low concentration. No attempt was made to resolve the optical isomers of IV or its oxide.

Isomers III and IV are particularly unusual because these are the first reported examples of two independent metal moieties attached to nonchelating triphos. The complex $Fe_2(CO)_2(C_5H_5)_2$(triphos), previously reported, is thought to be a biligated bimetallic type in which the end and center phosphorus atoms are bound to two iron atoms which are bridged by carbonyl groups.[10,15] Two metal atoms are also attached to triphos in the case of $Br(CO)_3Mn$(triphos)$Cr(CO)_5$[17] and $[(\eta^5\text{-}C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$,[15] but these contain chelated manganese. triphos may also chelate through the two end phosphorus atoms as has been proposed for *trans*-$[\eta^5\text{-}C_5H_5V(CO)_2(triphos)]$.[16]

Of the five complexes reported in this study, V can be

$$2(OC)_5WPPh_2H + (CO)_5WPPh(CH{=}CH_2)_2 \xrightarrow{KO(t\text{-}Bu)} \underset{V}{(OC)_5WPPh[CH_2CH_2PPh_2W(CO)_5]_2}$$

synthesized in highest yield, is most readily crystallized, and is the least soluble.

(14) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).
(15) R. B. King and J. C. Cloyd, Jr., *Inorg. Chem.*, **14**, 1550 (1975).
(16) I. Muller and D. Rehder, *J. Organomet. Chem.*, **139**, 293 (1977); G. Muhlbach, B. Rausch, and D. Rehder, *Ibid.*, **205**, 343 (1981).
(17) M. L. Schneider, N. J. Coville, and I. S. Butler, *J. Chem. Soc., Chem. Commun.*, 799 (1972); I. S. Butler and N. J. Coville, *J. Organomet. Chem.*, **80**, 235 (1974).

The ^{31}P NMR spectrum of V is a characteristic AB_2 type in appearance, much resembling that of the free ligand.[13] The satellite spectrum can be compared to that of $Ph_2P(Se)$-$CH_2CH_2P(Se)PhCH_2CH_2PPh_2(Se)$, which was recently analyzed.[18] It consists of the AB_2 part of an AB_2X spin system overlapping with the ABC part of an ABCX spin system. The center phosphorus resonance is found at 7.5 ppm ($^3J_{PP}$ = 34.7 Hz, J_{WP} = 239.4 Hz), and the terminal phosphorus atoms are found at 13.5 ppm (J_{WP} = 242.0 Hz).

In the course of this work we have found free radical additions to be useful and even preferred so long as at least one of the reactants is an uncoordinated phosphine. When both secondary phosphines and vinylphosphines were coordinated, the free radical method failed, but in those cases potassium *tert*-butoxide led to the desired addition. This observation has been noted in the preparation of diphos derivatives as well.[19]

The enormous potential of using addition reactions for ligation control becomes apparent in this study. Many complexes, until now considered chemical oddities because of their synthetic inaccessibility, will become commonplace and available for catalytic, mechanistic, and spectroscopic studies.

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Registry No. I, 79919-64-5; I (oxide), 79933-12-3; II, 79919-65-6; III, 79919-66-7; III (oxide), 79919-67-8; IV, 79919-68-9; IV (oxide), 79919-69-0; V, 79919-70-3; $(OC)_5WPPh_2CH_2CH_2PPh(O)$-$CH_2CH_2PPh_2$, 79919-71-4; $(OC)_5WPPh_2CH_2CH_2PPhCH_2CH_2$-$PPh_2(O)$, 79919-72-5; $(OC)_5WPPh_2CH_2CH_2PPh[W(CO)_5](CH=CH_2)$, 79933-13-4; $(OC)_5WPPh(CH=CH_2)_2$, 79919-73-6; $(OC)_5WPPh_2H$, 18399-62-7; $(OC)_5WPPh_2(CH=CH_2)$, 64012-10-8; PPh_2H, 829-85-6.

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Kinetics and Mechanism of Oxidative Addition of Methyl Iodide to Four- and Five-Coordinate Iridium(I) Complexes

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Oxidative addition of methyl iodide to four-coordinate iridium and rhodium complexes is important in the Monsanto process[1] in the conversion of methanol to acetic acid, which was found to be catalyzed by iodide ions.[2,3] We have lately found some more oxidative-addition reactions that are catalyzed by iodide ions.[4]

Our interest lies in the reactivities of five-coordinated d^8 iridium complexes. Recently we presented the first evidence of dioxygen attacking a five-coordinate iridium(I) iodide complex,[4] and we also obtained evidence for direct attack of dihydrogen on the five-coordinate complex $IrH(CO)(PPh_3)_3$.[5]

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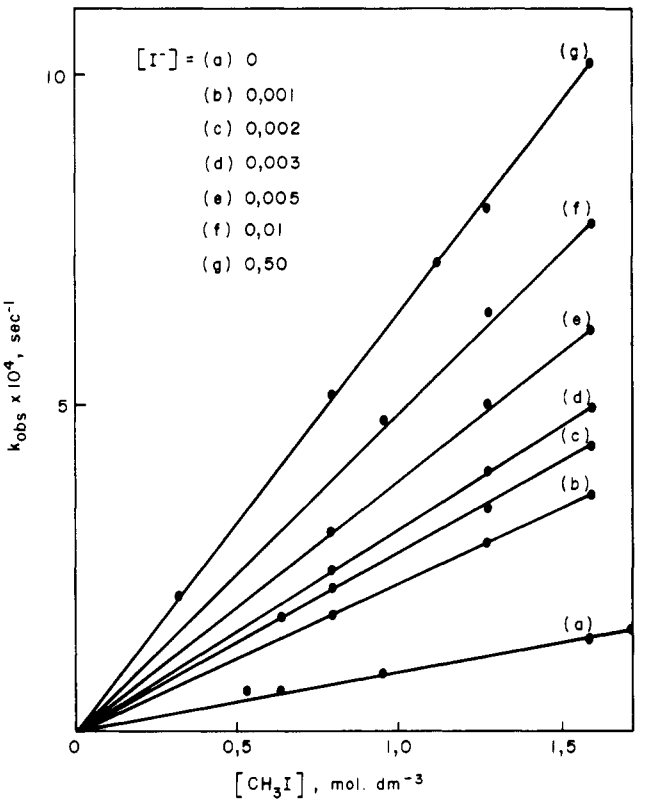

Figure 1. Plots of k_{obsd} vs. $[CH_3I]$ for different $[I^-]$ (in mol·dm^{-3}) at 25 °C. Experimental points were fitted to the theoretical lines obtained from the SPSS program.

We report here the kinetic results of the iodide-catalyzed reaction

$$[(cod)Ir(phen)]^+Cl^- + CH_3I \xrightarrow{[I^-]} [(cod)Ir(phen)(CH_3)(I)]^+ \quad (1)$$

(cod = cycloocta-1,5-diene; phen = 1,10-phenanthroline). The four-coordinate $[Ir(cod)(phen)]^+Cl^-$ in the presence of iodide establishes equilibrium 2 in methanol solution. A K_e value

$$[(cod)Ir(phen)]^+Cl^- + I^- \underset{MeOH}{\overset{K_e}{\rightleftharpoons}} (cod)Ir(phen)I \quad (2)$$

of 227 ± 5 cm^3·mol^{-1} (at 25 °C) was determined spectrophotometrically.

The rate of reaction 1 was found to be first order in both [complex] and [methyl iodide] and increased with increasing sodium iodide concentration. Under the conditions of the kinetic measurements all the reactions went to completion. Since the concentration of methyl iodide was always in sufficiently large excess to remain essentially constant throughout the reaction, the observed rate of disappearance of Ir(cod)-(phen)X (X = Cl, I) in every case studied yielded linear semilog graphs. The data at 20, 30, and 35 °C are given in Table I.

Plots of k_{obsd} vs. $[CH_3I]$ at different concentrations of iodide at 25 °C are shown in Figure 1. A family of straight lines through the origin for the methyl iodide concentration range used was obtained. The slopes of these plots increase with increasing [NaI]. All the data conform to the rate law given in eq 3, which can be derived from Scheme I.

$$k_{obsd} = \left(\frac{k_1 + k_2 K_e [I^-]}{1 + K_e [I^-]} \right) [CH_3I] \quad (3)$$

The rate law given in eq 3 simplifies to $k_{obsd} = k_1[CH_3I]$ if the concentration of added iodide is zero. The slope of plot (a) in Figure 1 then gives the values of k_1 (Table II), the rate

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