a catalyst structure where the noble metal is uniformly distributed throughout the polymer. Interfaces like that in Scheme II have also been fabricated by using Rh as the noble metal with aqueous $Rh_2(SO_4)_3$ as the reducible precursor.

The photoelectrochemical performance of a typical p-Si/$[(CoCpR_2^{+/0})_n]/Pd_{surf.}$ photocathode is shown in Figure 9. The steady-state photocurrent voltage curves are shown as a function of pH. Since the polymer has a pH-independent redox potential and $E°'(H^+/H_2)$ varies 59 mV/pH unit, there is an optimum pH for the photoelectrochemical generation of H_2: at high pH the reaction represented by eq 10 is not thermodynamically viable and at low pH the photovoltage is low. Note that the photovoltage, E_V, is measured by the extent to which H_2 generation (at 1 atm) can be effected at a more positive potential than $E°'(H^+/H_2)$. At pH ≈6.3, where the equilibrium constant for eq 10 would be about 1, the rate is too slow to give a large photocurrent, i_{photo}. Even at pH 6.0 (Figure 9), the driving force is insufficient to give a photocurrent that is proportional to light intensity. The efficiency is defined by eq 11. We find that the $[(CoCpR_2^{+/0})_n]/Pd$ catalyst

$$\eta\ (\%) = \frac{E_V i_{photo}}{\text{input optical power}} \times 100\% \qquad (11)$$

gives its highest efficiency at pH ≈4.5. No serious attempt has been made to optimize efficiency with this system, but the efficiencies for 632.8-nm illumination are about as good as with equivalent coverage of the viologen-based electron-relay system on p-Si photocathodes.[7] The pH-dependence of the photoelectrochemical efficiency shown in Figure 9 is consistent with the structure of the interface. Collectively, these experiments show that the use of I as a derivatizing reagent for photocathodes is viable. Recent experiments with p-InP/$[(CoCpR_2^{+/0})_n]/Rh_{surf.}$ show that significantly higher efficiencies (~10% for 632.8-nm illumination) can be obtained. The details of the surface chemistry of InP will be reported elsewhere.[32]

Conclusions

The cobaltocenium reagent I is a viable electrode derivatizing reagent for metallic and semiconducting materials. Both redox levels of $[(CoCpR_2^{+/0})_n]_{surf.}$ are rugged in aqueous solution. The redox potential, charge-transport rate, and metal-complex binding properties are similar to those of the viologen-based reagents previously studied in this laboratory. However, the polymer from I is more optically transparent and more durable at negative electrode potentials compared to the viologen-based reagents. Structured H_2 evolution catalyst systems can be prepared by using I, and the photoelectrochemical behavior accords well with the structure of the catalyst assembly.

In this work with $[(CoCpR_2^{+/0})_n]_{surf.}$ we have shown that it is possible to gain quantitative thermodynamic information regarding charge-compensating anion-exchange processes. Interestingly, a detailed study of the $Cl^-/Fe(CN)_6^{3-}$ and $Cl^-/Mo(CN)_8^{4-}$ systems shows that the selective uptake of the metal complexes is endothermic, $\Delta H° = +12$ kcal/mol for the $Fe(CN)_6^{3-}$, but there is a large, positive entropy change driving the process. The generality of this result will be tested in future experimentation.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research. Partial support from GTE Laboratories is also gratefully acknowledged.

Registry No. I, 97551-35-4; $IrCl_6^{2-}$, 16918-91-5; $IrCl_6^{3-}$, 14648-50-1; $Fe(CN)_6^{3-}$, 13408-62-3; $Fe(CN)_6^{4-}$, 13408-63-4; $Mo(CN)_8^{3-}$, 17845-99-7; $Mo(CN)_8^{4-}$, 17923-49-8; SnO_2, 18282-10-5; H_2O, 7732-18-5; H_2, 1333-74-0; Pt, 7440-06-4; Cl^-, 16887-00-6; Si, 7440-21-3.

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Relative Phosphorus Ligand Sizes from Cis:Trans Distributions of $W(CO)_4(L)(L')$ Products Obtained from the Reaction of $W(CO)_4(L)(py)$ with L′ (L and L′ = Phosphines), Reaction Kinetics, and Syntheses of Starting Materials

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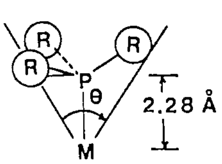
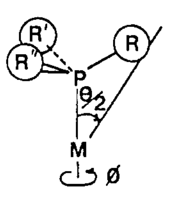
The relative sizes of 12 phosphines (L′ = PMe_3, $PPhMe_2$, PEt_3, $P(n\text{-}Bu)_3$, PPh_2Me, PPh_2Et, PPh_3, $P(p\text{-}tol)_3$, $PPh_2(i\text{-}Pr)$, $PPh_2(t\text{-}Bu)$, PBz_3, or PCy_3) have been studied by determining cis:trans ratios of $W(CO)_4(L)(L')$ products obtained from reactions of $W(CO)_4(L)(py)$ complexes with L′ (L = $PPhMe_2$, PPh_2Et, or $P(p\text{-}tol)_3$). In general, a decrease in the cis:trans ratio was observed as the Tolman cone angle of L′ increased. Exceptions occurred with PEt_3 and $P(n\text{-}Bu)_3$, for which cone angles of 140–145°, rather than Tolman's value of 132°, would be consistent with the other ratio data. Kinetic studies of these reactions indicate that dissociative loss of pyridine is rate limiting. Also reported are the synthesis of $W(CO)_4(L)(py)$ from $W(CO)_4(py)_2$ and L and ^{31}P NMR data for 21 new $W(CO)_4(L)(L')$ complexes.

Introduction

That phosphorus ligand sizes affect reactions involving transition metals to which they are attached is well documented.[1] A classic example of the purposeful use of ligand interactions is the asymmetric hydrogenation of prochiral olefins by Rh(I) catalysts.[2]

In order to quantify ligand sizes, Tolman introduced the concept of cone angle, θ.[3] In general, it is defined as the apex angle of a right cylindrical cone centered 2.28 Å from the center of a phosphorus atom that just touches the van der Waals radii of the outermost atoms. For unsymmetrical ligands, Tolman suggested use of half-cone angles, $\theta/2$.[1] These are defined as the angles between the metal–phosphorus vector and the vector that just touches the van der Waals radii of the outermost atoms.





Phosphorus ligands have been assigned quantitative size values through three techniques based on the cone angle concept. Tolman has used CPK models,[1,3] some groups (particularly Alyea and Ferguson)[4] have utilized X-ray crystallographic data, and we have

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(1) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(2) See, for example: (a) Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 99. (b) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.
(3) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

Table I. Analytical and Selected Spectroscopic Data for $W(CO)_4(L)(py)$ Complexes

	anal. found (calcd)				^{31}P NMR		
	% C	% H	% N	% Cl	δ^a	$^1J_{PW}$, Hz	$\nu(CO)$, cm^{-1}
$W(CO)_4(PMe_2Ph)(py)\cdot{}^1/_4CH_2Cl_2$	38.77	3.11	2.62	3.32	−12.5	232	2014 w, 1882 s, 1847 m
	(39.00)	(3.17)	(2.66)	(3.26)			
$W(CO)_4(PEtPh_2)(py)$	47.17	3.42	2.38		23.3	237	2006 w, 1882 s, 1846 m
	(46.88)	(3.42)	(2.38)				
$W(CO)_4(P(p\text{-tol})_3)(py)\cdot{}^1/_4CH_2Cl_2$	51.38	3.92	1.86		29.0	240	2020 w, 1980 s, 1850 m
	(51.86)	(3.81)	(2.00)	(2.53)			

[a] Relative to external 85% H_3PO_4. Downfield shifts are defined as positive.

used MINDO/3-[5] and MNDO-generated[6] optimized geometries. Each method has drawbacks, however. Tolman restricted himself to the single ligand conformation that produced the smallest cone angles. Alyea and Ferguson were similarly restricted to the single ligand conformations dictated in part by crystal-packing forces. Our computer modeling approach provided for the treatment of all unique ligand conformations and, consequently, allowed computation of weighted average cone angles based on conformer energy differences.[5] The studies were restricted by program and computer time limitations to relatively small molecules, however. Further, the relationships of any of the three approaches to dynamic, chemical systems is not clear.

We have reported a quantitative study of phosphorus ligand size effects based on a chemical reaction.[7] The distribution of *cis*- and *trans*-$W(CO)_4(L)_2$ products (L = PPh_2Me, PPh_2Et, $PPh_2(i\text{-}Pr)$, $PPh_2(t\text{-}Bu)$, PPh_3, $P(p\text{-tol})_3$ or $P(o\text{-tol})_3$) obtained from the reaction of $W(CO)_4(tmpa)$(tmpa = *N,N,N′,N′*-tetramethyl-1,3-propanediamine) with L were measured, and the cis:trans ratios were generally found to decrease as the cone angle of the ligand increased. The results were rationalized in terms of kinetic effects, whereby larger ligands were thought to react with apical pentacoordinate intermediates while smaller ligands reacted with the preferred[8] basal analogues. Dixon, Kola, and Howell have recently shown, however, that cis $\rightleftharpoons$ trans isomerization can be a facile process in these types of complexes and that the position of the equilibrium is dependent upon ligand sizes.[9] Thus, our observation that cis:trans ratios decrease as ligand sizes increase has been corroborated, but the source of that effect is thermodynamics (vide infra).

The $W(CO)_4(L)_2$ complexes, however, are of limited value for determining L sizes, since very small cis:trans ratios result from moderately sized ligands. For example, an equilibrium ratio of 0.11 was reported[9] for $P(n\text{-}Bu)_3$ (Tolman cone angle of 132°)[1] at 46 °C. A more generally applicable approach would be to make use of $W(CO)_4(L)(L')$ complexes, where L is a given phosphine and L′ is a series of phosphorus donor ligands. The appropriate selection of L could allow coverage of a range of L′ sizes. We therefore sought to develop a simple method for the preparation of large numbers of $W(CO)_4(L)(L')$ complexes and to determine whether these materials are useful for establishing sizes of ligands.

In this paper we report the syntheses of $W(CO)_4(L)(py)$ complexes (py = pyridine) from reaction 1 and cis:trans ratios of 29 product complexes obtained from reaction 2. Results from kinetic

$$W(CO)_4(py)_2 + L \rightarrow W(CO)_4(L)(py) + py \qquad (1)$$

$$W(CO)_4(L)(py) + L' \rightarrow W(CO)_4(L)(L') + py \qquad (2)$$

studies of reaction 2 are also reported. The starting materials, $W(CO)_4(L)(py)$, were selected because they seemed to provide a reasonable compromise among the desirable characteristics of stability, ease of preparation, and ready loss of leaving group.

Experimental Section

Benzene was dried by refluxing and distilling over sodium under a nitrogen atmosphere. Pyridine was dried over and distilled from KOH under a nitrogen atmosphere. All phosphine ligands were purchased from Strem Chemicals, Inc., and used as received. Chromatography solvents were purged with N_2 for at least 0.5 h. All reactions, column chromatographic separations, and manipulations involving free phosphorus ligands were performed under a nitrogen atmosphere. The $W(CO)_4(py)_2$ starting material was prepared by the method of Cotton and Kraihanzel.[10]

Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, IN. ^{31}P NMR spectra were obtained from a Varian FT-80A spectrometer operating at 32.197 MHz in the Fourier transform mode. Instrumental parameters included 8065-Hz spectral widths, broad-band proton decoupling (1000 Hz), acquisition times of 1.015 s, 16 383 data points, 20° flip angles (pulse width of 4 μs), and a Fourier number of 16 384. Typically, 2000 transients were accumulated on samples containing 60 mg of complex dissolved in 3 mL of 20% benzene-d_6/80% benzene in a 10-mm tube. Except for the kinetic studies, spectra were obtained at the ambient probe temperature (31 °C). Infrared data were obtained from a Beckman 4250 instrument using CH_2Cl_2 solutions.

$W(CO)_4(L)(py)$ Complexes. The following procedure is for L = PPh_2Et (**2**), but the other complexes were prepared similarly. To 598 mg (1.32 mmol) of $W(CO)_4(py)_2$ contained in a 100-mL round-bottomed flask equipped with a magnetic stirring bar were added 75 mL of benzene and 250 μL (ca. 1.3 mmol) of PPh_2Et. The stoppered flask was maintained at 40 °C with magnetic stirring for 24 h. Not all of the $W(CO)_4(py)_2$ complex dissolved initially, but by the end of the 24-h period the solution was clear. The benzene was then removed under vacuum. The complexes can be recrystallized from a chloroform/methanol mixture to yield bright yellow crystals. Unreacted $W(CO)_4(py)_2$ tends to contaminate the product if it is not chromatographed, however.

Chromatographic purification was accomplished on the crude reaction product by using silica gel in a 20-cm column with an inner diameter of 2.5 cm. A 90% hexane/10% CH_2Cl_2 mixture was used as eluant until the faint band of $W(CO)_4(L)_2$ complex had traveled about two-thirds of the length of the column. The solvent mixture was then changed to 75% hexane/25% CH_2Cl_2 to increase the rate of complex elution. Total yields after chromatography were 76%, 78%, and 75% for **1**, **2**, and **3**, respectively. Analytical samples were prepared from chromatographic fractions by evaporation of about 80% of the elution solvent under a stream of nitrogen, which resulted in the formation of fine needles. After decantation of the remaining solvent, the crystals were dried under dynamic vacuum for at least 24 h. Microanalytical, ^{31}P NMR, and IR data are listed in Table I. (The ^1H NMR spectra of **1** and **3** showed a peak consistent with $^1/_4$ mol of CH_2Cl_2.)

$W(CO)_4(L)(L')$ Complexes. The following description is for the reaction of PPh_2Et with $W(CO)_4[P(p\text{-tol})_3](py)$ (**3**) on a preparative scale. The reactions of **3** with $PPhMe_2$, **1** with PPh_2Et and $P(p\text{-tol})_3$, and **2** with $PPhMe_2$ and $P(p\text{-tol})_3$ were performed similarly. The remaining complexes listed in Table II were obtained by the method described under the subheading cis:trans Ratio Determinations. To 491 mg (0.72 mmol) of **3** dissolved in 35 mL of benzene contained in a 50-mL round-bottomed flask equipped with a magnetic stirring bar was added 170 μL (ca. 0.86 mmol) of PPh_2Et. The stoppered flask was maintained at 40 °C with magnetic stirring until the reaction was complete as indicated by thin-layer chromatography (ca. 15–20 days for L = PPh_2Et or $P(p\text{-tol})_3$, 4 weeks for L = PMe_2Ph). Silica gel with either 90% hexane/10% CH_2Cl_2 or 95% hexane/5% ethyl acetate as elution solvent is satisfactory. R_f values for $W(CO)_4(py)_2$, $W(CO)_4(L)(py)$, and $W(CO)_4(L)_2$ in the former system are 0, 0.1, 0.3 and 0.4, and 0.6, respectively. Corresponding values in the latter system are 0, 0.1, 0.4 and 0.5, and 0.6, respectively. The benzene was then removed to yield the crude product. ^{31}P NMR data are listed in Table II.

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(10) Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 533.

Table II. ^{31}P NMR Data for W(CO)$_4$(L)(L′) Complexes

compd	L	L′	δ(L)[a]		δ(L′)[a]		$^2J_{PP}$, Hz	
			cis	trans	cis	trans	cis	trans
4	PPhMe$_2$	PMe$_3$	−25.4	−19.7	−40.7	−35.2	24	42
5	PPhMe$_2$	PPhMe$_2$	−25.3[b]	−19.7				
6	PPhMe$_2$	PEt$_3$	−27.3	−20.5	−1.3	6.5	23	44
7	PPhMe$_2$	P(*n*-Bu)$_3$	−27.3	−20.0	−9.1	−1.1	24	44
8	PPhMe$_2$	PPh$_2$Me	−25.6	−20.0	−3.9	2.6	22	47
9	PPhMe$_2$	PPh$_2$Et	−26.4	−20.1	12.8	19.0	23	48
10	PPhMe$_2$	P(*p*-tol)$_3$	−25.3	−19.9	20.5	25.6	23	50
11	PPhMe$_2$	PPh$_2$(*i*-Pr)	−26.8	−20.1	26.8	34.2	24	50
12	PPhMe$_2$	PPh$_2$(*t*-Bu)	−26.0	−20.2	43.8	49.9	22	52
13	PPhMe$_2$	PBz$_3$	−26.1	−21.0	−4.3	9.2	24	55
14	PPhMe$_2$	PCy$_3$	−29.8	−17.9	28.7	37.4	25	49
15	PPh$_2$Et	PMe$_3$	12.8	19.3	−41.9	−35.1	22	47
16	PPh$_2$Et	PEt$_3$	10.9	18.0	−3.5	4.1	21	48
17	PPh$_2$Et	P(*n*-Bu)$_3$	11.0	18.0	−11.4	−2.8	22	48
18	PPh$_2$Et	PPh$_2$Me	12.3	18.2	−4.9	1.8	22	53
19	PPh$_2$Et	PPh$_2$Et	11.4[c]	17.8[c]				
20	PPh$_2$Et	PPh$_3$	11.2	17.3	22.0	27.6	23	55
21	PPh$_2$Et	P(*p*-tol)$_3$	11.4	17.7	19.2	24.6	23	54
22	PPh$_2$Et	PPh$_2$(*i*-Pr)	10.6	17.6	24.4	31.9	22	53
23	PPh$_2$Et	PPh$_2$(*t*-Bu)	10.6	16.8	41.7	47.8	23	55
24	P(*p*-tol)$_3$	PMe$_3$	20.6	25.9	−41.0	−34.7	23	48
25	P(*p*-tol)$_3$	PEt$_3$	19.3	24.9	−3.5	4.5	23	49
26	P(*p*-tol)$_3$	P(*n*-Bu)$_3$	19.3	24.9	−11.0	−3.2	23	49
27	P(*p*-tol)$_3$	PPh$_2$Me	20.3	24.9	−4.1	2.0	22	53
28	P(*p*-tol)$_3$	P(*p*-tol)$_3$	19.7[c]	24.7[c]				
29	P(*p*-tol)$_3$	PPh$_2$(*i*-Pr)	18.4	24.5	25.3	31.8	24	55
30	P(*p*-tol)$_3$	PPh$_2$(*t*-Bu)	18.6	24.2	41.6	47.8	21	57
31	P(*n*-Bu)$_3$	P(*n*-Bu)$_3$	−10.1[d]	−2.6[d]				
32	PPh$_2$Me	PPh$_2$Me	−4.3[c]	1.7[c]				

[a] Relative to 85% H$_3$PO$_4$. Downfield shifts are defined as positive. [b] Literature value of −25.8 (McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.) [c] Previously reported values[7] are 2.4 ppm too shielded. [d] Literature values of δ −10.4 and −2.6 for cis and trans, respectively (reference cited in footnote *b*, above) and −10.0 and −2.5. (Grim, S. O.; Wheatland, D. A. *Inorg. Chem.* **1969**, *8*, 1716.)

Column chromatography on silica gel using either 90% hexane/10% CH$_2$Cl$_2$ or 95% hexane/5% ethyl acetate with the column described above readily separated the bis(phosphine) product complexes from the starting materials. However, significant intermolecular rearrangements apparently took place during chromatography (see Results and Discussion).

Kinetic Studies. For the study of the dependence of reaction rates upon ligand concentrations, 200.5 mg (0.340 mmol) of **2** were dissolved in a sufficient mixture of 20% benzene-*d*$_6$/80% benzene to make a total volume of 12.00 mL. The resulting 0.0284 M solution was divided into four equal portions to which 36.4 mg (0.170 mmol), 72.8 mg (0.340 mmol), 145.7 mg (0.681 mmol), or 291.4 mg (1.362 mmol) of PPh$_2$Et was added. The solutions were maintained at 40.0 °C. ^{31}P NMR spectra were obtained from each solution at ca. 1, 25, 49, 73, 97, and 169 h. Except for a probe temperature of 40 °C, the instrumental parameters were the same as those described above. Concentrations of the complexes were calculated from integrals of the spectra by using the fact that the sum of the tungsten reactant and product equaled 0.0284 M. The k_{obsd} values were computed from the slope obtained by least-square fits of the plots of ln [**2**] vs. time.

Studies of the dependence of reaction rates upon ligand type were performed similarly. Thus, 192.0 mg (0.326 mmol) of **2** were dissolved in sufficient 20% benzene-*d*$_6$/80% benzene to give 12.00 mL of 0.0272 M solution. Ligand quantities of 65.9 mg (0.326 mmol) of P(*n*-Bu)$_3$, 45.0 mg (0.326 mmol) of PPhMe$_2$, or 69.8 mg (0.326 mmol) of PPh$_2$Et were added to 3.00 mL aliquots of the above solution. The solutions were maintained at 40 °C. ^{31}P NMR spectra were obtained at ca. 0.2, 24, 48, 72, 96 and 168 h with a probe temperature of 40 °C. Concentrations were determined by integration of those parts of the ^{31}P NMR spectra due to **2** and the portion of W(CO)$_4$(PPh$_2$Et)(L′) arising from PPh$_2$Et. (It was assumed that the NOE on the ^{31}P NMR signals from **2** were the same as those from PPh$_2$Et in the product complexes). The k_{obsd} values were computed from the slopes obtained from the least-squares fits of plots of ln [**2**] vs. time.

Qualitative rate data for cis ⇌ trans isomerization reactions were obtained for W(CO)$_4$L$_2$ complexes, where L = PPhMe$_2$, PPh$_2$Me and P(*p*-tol)$_3$. For each, approximately 70 mg (0.16 mmol) of W(CO)$_4$(tmpa)[11] (tmpa = *N,N,N′,N′*-tetramethyl-1,3-propanediamine) was dissolved in 3 mL of 20% benzene-*d*$_6$/80% benzene and ca. 1.6 mmol of ligand added. The reaction solutions were maintained at 40 °C and ^{31}P NMR spectra (probe temperature of 40 °C) obtained for each at ca. 0.5, 1.5, 3, 5, 7, 24 and 48 h. Ligand:total product and cis:trans product ratios were obtained from integration of the spectra.

Cis:Trans Ratio Determinations. Typically, 50 to 75 mg of W(CO)$_4$(L)(py) complex were dissolved in 10 mL of benzene, four to five times the molar quantity of appropriate ligand was added, and the mixture was maintained at 40 °C. After 14 days (L = PPhMe$_2$) or 7 days (L = PPh$_2$Et or P(*p*-tol)$_3$), the benzene was removed under vacuum, the entire crude product was dissolved in 3 mL of 20% benzene-*d*$_6$/80% benzene, and ^{31}P NMR spectra were obtained (ca. 20% of the starting material had not yet reacted). The cis:trans ratios were computed from integrals of these spectra. Each ratio was calculated from both the L and L′ portions of the spectra, and the results were averaged. These are presented in Table III. Most of the reactions were performed twice by two different people, and each integral ratio was computed independently by a second person. Generally, duplicate results were within 10% of the values listed in Table III.

Results and Discussion

Preparation of W(CO)$_4$(L)(py) Complexes (Reaction 1). The reaction of W(CO)$_4$(py)$_2$ in a 1:1 mole ratio with one of the three phosphines PPhMe$_2$, PPh$_2$Et, or P(*p*-tol)$_3$ in benzene or methylene chloride proceeded smoothly and completely in 1 day at 40 °C to provide the air-stable complexes W(CO)$_4$(L)(py) (**1**, **2**, and **3**, respectively). Yields after chromatography (see Experimental Section) were 75–80%. Analytical and selected spectroscopic data are listed in Table I. On the basis of the infrared spectrum and the single ^{31}P NMR resonance (excluding ^{183}W satellites), each complex was assigned a cis geometry. As noted originally by Darensbourg and Kump[12] for the analogous reaction with PPh$_3$, substitution of the first pyridine occurs rapidly compared to substitution of the second. Consequently, the formation of W(CO)$_4$(L)$_2$ was found to be minimal for these three ligands, being less that 10% of the crude product. Increasing the reaction temperature to 60 °C increased the reaction rate, but also increased the amount of W(CO)$_4$(L)$_2$ complex formed.

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Table III. Cis:Trans $W(CO)_4(L)(L')$ Product Ratios from the Reaction of $W(CO)_4(L)(py)$ with L′

L	L′	cis:trans	$\delta(^{31}P)$ of L in *cis*-$W(CO)_4(L)(L')$
$PPhMe_2$	PMe_3	10.4	−25.4
$PPhMe_2$	$PPhMe_2$	8.0	−25.3
$PPhMe_2$	PEt_3	1.6	−27.3
$PPhMe_2$	$P(n\text{-}Bu)_3$	1.5	−27.3
$PPhMe_2$	PPh_2Me	3.4	−25.6
$PPhMe_2$	PPh_2Et	2.0	−26.4
$PPhMe_2$	$P(p\text{-}tol)_3$	2.2	−25.3
$PPhMe_2$	$PPh_2(i\text{-}Pr)$	2.2	−26.8
$PPhMe_2$	$PPh_2(t\text{-}Bu)$	0.82	−26.0
$PPhMe_2$	PBz_3	0.61	−26.1
$PPhMe_2$	PCy_3	0.43	−29.8
PPh_2Et	PMe_3	2.7	12.8
PPh_2Et	$PPhMe_2$	2.5	12.8
PPh_2Et	PEt_3	0.35	10.9
PPh_2Et	$P(n\text{-}Bu)_3$	0.36	11.0
PPh_2Et	PPh_2Me	1.0	12.3
PPh_2Et	PPh_2Et	0.33	11.4
PPh_2Et	PPh_3	0.30	11.2
PPh_2Et	$P(p\text{-}tol)_3$	0.33	11.4
PPh_2Et	$PPh_2(i\text{-}Pr)$	0.34	10.6
PPh_2Et	$PPh_2(t\text{-}Bu)$	0.19	10.6
$P(p\text{-}tol)_3$	PMe_3	2.8	20.6
$P(p\text{-}tol)_3$	$PPhMe_2$	2.2	20.5
$P(p\text{-}tol)_3$	PEt_3	0.30	19.3
$P(p\text{-}tol)_3$	$P(n\text{-}Bu)_3$	0.33	19.3
$P(p\text{-}tol)_3$	PPh_2Me	1.2	20.3
$P(p\text{-}tol)_3$	PPh_2Et	0.30	19.2
$P(p\text{-}tol)_3$	$P(p\text{-}tol)_3$	0.27	19.7
$P(p\text{-}tol)_3$	$PPh_2(i\text{-}Pr)$	0.25	19.4
$P(p\text{-}tol)_3$	$PPh_2(t\text{-}Bu)$	0.26	18.6

The reaction with larger phosphines provided different results, however. Ligands with greater cone angles appear to accelerate loss of the second pyridine ligand, yielding substantial quantities of $W(CO)_4(L)_2$ complexes. For example, attempts to prepare $W(CO)_4(PCy_3)(py)$ provided $W(CO)_4(PCy_3)_2$ and $W(CO)_4(py)_2$ with no evidence for the desired complex. Increased rates of cis ligand dissociation with increased phosphine size have been observed previously in both mononuclear[13,14] and cluster[15] carbonyl complexes.

Preparation of $W(CO)_4(L)(L')$ Complexes (Reaction 2). The $W(CO)_4(L)(L')$ complexes listed in Table II were obtained from the reaction of a $W(CO)_4(L)(py)$ complex with the appropriate L′ ligand at 40 °C in benzene. Both infrared (ν(CO)) and ^{31}P NMR spectra are consistent with *cis*- and *trans*-$W(CO)_4(L)(L')$ complexes.[16] Complexes **9**, **10**, and **21** were each prepared by the two sequences of ligand additions that are possible through reactions 1 and 2. For example, **9** was obtained by the addition of $PPhMe_2$ to **2** and by the conjugate reaction of PPh_2Et with **1**. The ^{31}P NMR data presented in Table II are analogous to the findings of Schenk and Buchner[17] for similar complexes, where the trans compounds display chemical shifts that are deshielded and $^2J_{PP}$ coupling constants that are larger than those of the cis isomers.

Reaction 2 is slow at 40 °C when L is a comparatively small ligand such as PPh_2Et (see the Kinetic Studies subsection for rate constants). Raising the temperature to 80 °C reduces the reaction time by about a factor of 3 but is also accompanied by reduction of ca. 5–10% in yields. Some $W(CO)_4(L)_2$ and/or $W(CO)_4(L')_2$ (generally less than 10% of the desired product) was obtained from all of the reactions even when oxygen was carefully excluded. Since only $W(CO)_4(L)(py)$ was observed in the ^{31}P NMR spectra of the starting materials, intermolecular rearrangements appear to be the sources of the byproducts. When the reaction solutions were allowed to come into contact with air, the quantities of symmetrically substituted complexes increased, an unidentified brown solid precipitated, and, concomitantly, the yields of desired unsymmetrically substituted products were significantly reduced.

The progress of reaction 2 is readily monitored by thin-layer chromatography. (See Experimental Section for R_f values.) With 95% hexane/5% ethyl acetate or 90% hexane/10% CH_2Cl_2, two spots were observed for the $W(CO)_4(L)(L')$ complexes. When 75% hexane/25% CH_2Cl_2 was used as eluant, the faster moving spot overlapped with that from the free ligand giving a broader spot with an R_f value of 0.6–0.7.

Although it is tempting to conclude that the two thin-layer spots from $W(CO)_4(L)(L')$ complexes are due to pure cis and pure trans isomers, the situation is actually more complex than that. Column chromatography of the crude product mixtures on silica gel using either 95% hexane/5% ethyl acetate or 90% hexane/10% CH_2Cl_2 also provided two bands. As evinced by ^{31}P NMR spectra, the second contained primarily cis species, but included both unsymmetrically and symmetrically substituted complexes (i.e., $W(CO)_4(L)(L')$, $W(CO)_4(L)_2$ and $W(CO)_4(L')_2$). The first band also consisted of unsymmetrical and symmetrical complexes but was largely composed of trans isomers. Since the combined fractions contained more symmetrically substituted complexes (ca. 25%) than the original sample prior to chromatography (less than 10%), it appears that intermolecular rearrangments occurred on the column. Further, the rate of cis $\rightleftharpoons$ trans isomerization is sufficiently rapid near room temperature (vide infra) to preclude isolation of pure isomers by chromatography. The total yields of disubstituted complexes after chromatography were generally 70–80%.

The preparative route to unsymmetrically substituted complexes described here can offer advantages over previously described procedures such as those shown in reactions 3–5.[17,18] The $W(CO)_4(py)_2$ starting material[10] and the $W(CO)_4(L)(py)$ intermediates are easily prepared in quantity, are not hygroscopic, and are air stable as solids. Further, the preparations of $W(CO)_4(L)(L')$ complexes from $W(CO)_4(py)_2$ can be accomplished in a single-pot, two-step process. The procedure is also a reasonable alternative for use with ligands that are incompatible with the conditions of reactions 3–5 or with the preparation of their starting materials. Thus, ligands that are readily attacked by oxidizing agents (i.e. ONR_3, which is a convenient reagent for the preparation of $W(CO)_4(L)(CH_3CN)$),[19] protic solvents, or Ag^+ can be used with this method. The primary disadvantage is the apparently unavoidable production of some symmetrically substituted complexes from reaction 2.

$$[W(CO)_4LX]^- + Ag^+ + L' \rightarrow W(CO)_4(L)(L') + AgX \qquad (3)$$

$$[W(CO)_4LX]^- + L' \xrightarrow[\text{protic solvent}]{} W(CO)_4(L)(L') + X^- \qquad (4)$$

$$W(CO)_4(L)(CH_3CN) + L' \rightarrow W(CO)_4(L)(L') + CH_3CN \qquad (5)$$

Kinetic Studies. Four reactions of $W(CO)_4(PPh_2Et)(py)$ (**2**) with PPh_2Et at 40 °C in benzene were monitored by ^{31}P NMR spectroscopy. The initial concentration of **2** was 0.0284 M for all four reactions; ligand concentrations provided complex to ligand ratios of 1:2, 1:4, 1:8, and 1:16. Plots of ln [**2**] vs. time were linear in all cases with correlation coefficients of >0.999, >0.999, 0.995, and 0.991, respectively. The four values of k_{obsd} computed from the slopes are similar (2.08, 2.34, 2.61, and 2.81 $\times 10^{-6}$ s^{-1}, respectively), although there is a general increase with increased ligand concentration. These results strongly suggest that the reaction is first order in complex and predominantly zero order in ligand under these conditions.[20] Within experimental error,

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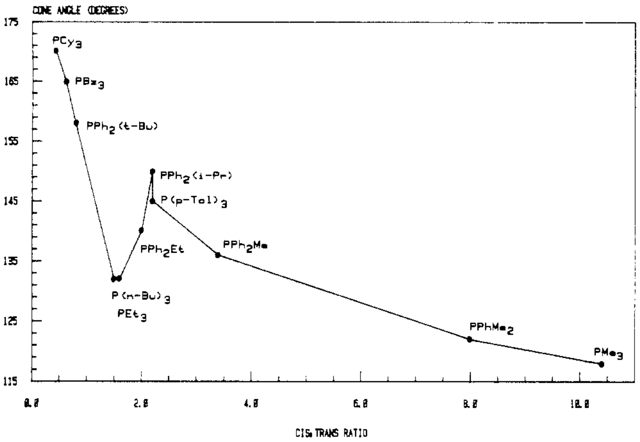

Figure 1. Plot of L′ cone angle vs. cis:trans ratio for $W(CO)_4(L)(L')$, L = $PPhMe_2$.

cis:trans product ratios were the same for all four reactions. Similarly, data from the reactions of **2** with $P(n\text{-}Bu)_3$, $PPhMe_2$, or PPh_2Et (40 °C, benzene solutions, 0.0272 M in **2**, 0.109 M in ligand) provided linear plots of ln [**2**] vs. time (correlation coefficients of 0.996, >0.999, and >0.999, respectively). The similarity of the k_{obsd} values (2.24, 2.33, and 2.06 × 10^{-6} s^{-1}) is consistent with a lack of dependence upon the reacting ligand. These results are analogous to those recently reported for the substitution of py in $Mo(CO)_4(py)_2$ by chelating diamines.[21]

The reaction rates of **1** with PPh_2Et or $P(p\text{-}tol)_3$ and **3** with $PPhMe_2$ or PPh_2Et were observed qualitatively by using thin-layer chromatography. They were found to be highly dependent upon the ligand, L, initially attached to tungsten. Thus at 40 °C in benzene, the reactions of $W(CO)_4(PPhMe_2)(py)$ were about half as fast as those of $W(CO)_4[P(p\text{-}tol)_3](py)$. The latter were comparable or slightly faster than those of $W(CO)_4(PPh_2Et)(py)$. These results are consistent with previously reported phosphine steric accelerations of cis ligand dissociations.[13-15]

Ligand Steric Effects. Cis:trans ratios of 29 $W(CO)_4(L)(L')$ products were determined via ^{31}P NMR spectroscopy for 32 reactions. The ratios are listed in Table III; spectroscopic data are given in Table II. The reactions belonged to one of the series (6)–(8). These included the six that constitute the three possible

$$W(CO)_4(PPhMe_2)(py) + L' \rightarrow W(CO)_4(PPhMe_2)(L') + py \quad (6)$$

$$W(CO)_4(PPh_2Et)(py) + L' \rightarrow W(CO)_4(PPh_2Et)(L') + py \quad (7)$$

$$W(CO)_4[P(p\text{-}tol)_3](py) + L' \rightarrow W(CO)_4[P(p\text{-}tol)_3](L') + py \quad (8)$$

conjugate reaction pairs (e.g., the pair of reaction 6 with L′ = PPh_2Et and reaction 7 with L′ = $PPhMe_2$).

Tolman cone angle values[1] vs. cis:trans ratios are plotted in Figures 1–3 for reactions 6–8, respectively. No significance should be attached to lines connecting the points; they are included merely to help identify tendencies. With the exception of PEt_3 and $P(n\text{-}Bu)_3$, which are discussed separately below, the general trend of decreased cis:trans ratio with increased ligand size is consistent on all three plots. For a given reactant ligand, L′, the ratios are greatest from reaction 6 and similar for reactions 7 and 8. No correlation was found between cis:trans ratios and the Tolman electronic parameter (ν) values,[1] and as mentioned in the previous subsection, the ratios are independent of the quantity of L′ ligand used. These results suggest that cis:trans ratios can be a very sensitive indicator of phosphorus ligand sizes.

Limitations also need to be noted. Some scatter of points can be seen in Figures 2 and 3 at low cis:trans ratios. This is probably due in part to integral measurement errors, which become increasingly critical as the difference in peak areas becomes greater. There also seems to be a leveling effect when cis:trans ratios reach about 1:3. It would appear, therefore, that the method should only be used when ratios lie between about 1:3 and 3:1. This is not as restrictive as it might seem, since the composite range covered by L = $PPhMe_2$ and PPh_2Et include L′ cone angles from about 170° (L = $PPhMe_2$, cis:trans ratio of 0.43) to about 120° (L = $P(p\text{-}tol)_3$ or PPh_2Et, cis:trans ratio of about 2.8). Furthermore, it is likely that the range could be extended to both smaller and larger ligands by selection of appropriate counterligands.

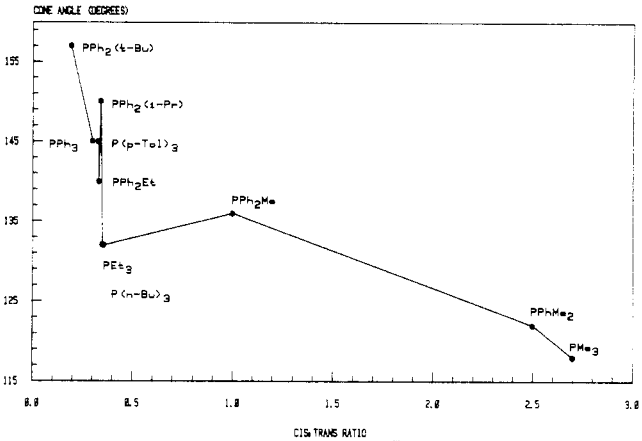

Figure 2. Plot of L′ cone angle vs. cis:trans ratio for $W(CO)_4(L)(L')$, L = PPh_2Et.

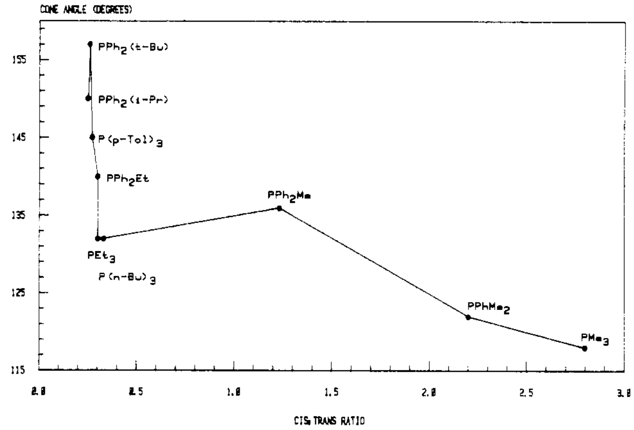

Figure 3. Plot of L′ cone angle vs. cis:trans ratio for $W(CO)_4(L)(L')$, L = $P(p\text{-}tol)_3$.

The source of the steric effect is thermodynamics. Dixon, Kola, and Howell[9] have reported that the reaction of $W(CO)_4(nbd)$ with L (nbd = norbornadiene; L = $P(n\text{-}Bu)_3$, $P(OMe)_3$, or $P(OPh)_3$) produced primarily (perhaps totally) cis product initially, which subsequently isomerized intramolecularly to provide equilibrium concentrations of cis- and trans-$W(CO)_4(L)_2$. For L = $P(n\text{-}Bu)_3$, the rate constant for the cis → trans rearrangement was 3.10 × 10^{-4} s^{-1} at 46 °C. Rates of isomerism were found to be dependent upon both the steric and electronic properties of L. Thus, for $P(OMe)_3$ and $P(OPh)_3$, the corresponding constants were 1.42 × 10^{-4} at 65 °C and 2.52 × 10^{-4} at 93.5 °C, respectively.

We measured the cis:trans ratios of $W(CO)_4(PPh_2Et)(L')$ products during the kinetic studies of $W(CO)_4(PPh_2Et)(py)$ + L′ (L′ = $P(n\text{-}Bu)_3$, PPh_2Et, or $PPhMe_2$). A slight decrease in ratio with time may have occurred for all three ligands, but ratios were within our estimates of integral measurement errors. Since the time period of these studies included only a little over 2 half-lives, we also examined the reactions of $W(CO)_4(PPhMe_2)(py)$ with PPh_2Et or $P(n\text{-}Bu)_3$ for longer periods (about 6 to 7 half-lives). Again, within our estimates of experimental error, the cis:trans ratios were essentially the same throughout the latter reactions. These results are consistent with a rate of

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(20) Rate laws of the type (k_1 + k_2[L])[complex] have been observed previously in related systems. See, for example: Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 1089 and references therein.

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isomerization being much faster than the rate of reaction, since k for cis → trans of $W(CO)_4[P(n\text{-}Bu)_3]_2$ has been reported[9] as 3.10×10^{-4} s^{-1} at 46 °C and we found k_{obsd} for $W(CO)_4(PPh_2Et)(py) + L'$ to be about 2.4×10^{-6} s^{-1}.

To prove this, the reactions of $W(CO)_4(tmpa)$ with PPh_2Me, $PPhMe_2$, or $P(p\text{-tol})_3$ were observed by ^{31}P NMR spectroscopy. These studies were chosen because $W(CO)_4(tmpa)$ reacts quite rapidly with phosphorus donors,[11,22] and of the ligands we commonly used, these represent extremes of electronic differences as measured by the Tolman ν values (PPh_2Me, 2067 cm^{-1}),[1] and large and small Tolman cone angles ($PPhMe_2$ = 122°, $P(p\text{-tol})_3$ = 145°).[1] For PPh_2Me and $PPhMe_2$, only the cis-$W(CO)_4(L)_2$ products were observed initially, but within 24 h each had reached its equilibrium distribution. Both cis- and trans-$W(CO)_4(L)_2$ complexes were observed early in the reaction of $P(p\text{-tol})_3$, but the cis complexes predominated. Again, within 24 h the equilibrium distribution was observed. These results suggest that two scrambling processes may occur. In addition to the slow intramolecular rearrangement of $W(CO)_4L_2$ suggested by Dixon, Kola, and Howell,[9] a fast process is also possible that likely involves the five-coordinate $W(CO)_4L$ intermediate.[22b] ((η^1-tmpa)$W(CO)_4(L)$ species have been isolated and found to be exclusively cis.)[22a]

The important conclusions from these studies are that, *for the combination of ligands reported here*, the rates of isomerization are fast compared to the rates of reaction and our reported cis:trans ratios reasonably approximate the equilibrium values. There is a potential problem in extending our approach to ligands that are electronically very different from those included here, however. We chose a system that made use of a readily prepared, very stable starting material. The trade-off was slow subsequent reactions. To avoid excessively long reaction periods, we interrupted the reactions after only about 2 half-lives. Consequently, if the ligands being used were to cause slow cis → trans isomerizations, the cis:trans ratios measured at the point of interruption might not be close to the equilibrium distributions. Although this was not a difficulty with the phosphines reported here, the use of phosphites could be a problem (viz., k for cis → trans in $W(CO)_4[P(OPh)_3]_2$ was reported as 2.52×10^{-4} s^{-1} at 93.6 °C).[9] We are in the process of studying ligands such as phosphites that have much larger Tolman ν values.

A final point that needs addressing is the consistently different behavior of PEt_3 and $P(n\text{-}Bu)_3$ compared to that of the other ligands (see Figures 1–3). Two explanations are possible: there is an inherent problem with the experimental approach we used that is only apparent with these ligands, or the cone angle values for these two are underestimated by about 10° on the basis of Tolman's approach. The former is addressed first.

Both PEt_3 and $P(n\text{-}Bu)_3$ are more basic and have smaller Tolman ν values than most of the ligands used in this study. As described above, we believe that the cis:trans distributions reported here are sufficiently close to the equilibrium values that the behavior of PEt_3 and $P(n\text{-}Bu)_3$ is not due to their having reached equilibrium while all others have not. (Dixon, Kola, and Howell found that the rate of isomerization increased with decreasing ν value.) Another possibility is that the cis ⇌ trans equilibria are substantially affected by electronic as well as steric properties. Our results suggest this is not the case either, however. For example, the fact that the cis:trans ratios of $W(CO)_4(PPh_2Et)[P(p\text{-tol})_3]$ and $W(CO)_4(PPh_2Et)(PPh_3)$ products are within experimental error is consistent with $P(p\text{-tol})_3$ and PPh_3 steric effects (the Tolman cone angles are identical[1]) and not with their electronic properties (Tolman ν values of 2066.6 vs. 2069.0 cm^{-1}, respectively[1]). Further, PMe_3 does not behave like PEt_3 and $P(n\text{-}Bu)_3$ but is in line with the other ligands.

Therefore, we are inclined to believe that the cone angles of PEt_3 and $P(n\text{-}Bu)_3$ are underestimated by about 10° using Tolman's approach. Tolman assigned cone angles to ligands on the basis of the single conformation that provided the smallest value. Other conformations undoubtedly contribute, but as long as those contributions are similar for a series of ligands, the relative ligand sizes will be predicted correctly. The smallest half-cone angle for an alkyl group other than methyl is obtained by folding the $P\text{–}CH_2\text{–}R$ chain back so that R is trans to the phosphorus lone pair of electrons, but this conformation is believed to be higher in energy than when R is gauche.[23] Consequently, as the number of alkyl groups is increased, the importance of other conformations also increases, and the size of the ligand is increasingly underestimated by Tolman's method.

Further evidence that PEt_3 and $P(n\text{-}Bu)_3$ are underestimated comes from our work as well as previous reports. Chalk and Pomeroy[14] have reported $\Delta S^{\ddagger}$ values for the reaction of $(CO)_3Ru(L)(SiCl_3)_2$ with L′ to yield $(CO)_2Ru(L)(L')(SiCl_3)_2$ (L and L′ are phosphorus ligands). Their plot of $\Delta S^{\ddagger}$ vs. cone angle would be improved if a 140–145° value were used for $P(n\text{-}Bu)_3$. Similarly, Tolman's plot of ligand binding ability on Ni(0) vs. cone angle (Figure 7 of ref 1) would be improved if $P(n\text{-}Bu)_3$ and PEt_3 had 142° cone angles. The ^{31}P NMR chemical shifts from our cis complexes also suggest that a larger cone angle value is appropriate. Although chemical shifts of phosphorus compounds are dependent upon several variables,[24] it has been observed that replacement of a cis CO group from $W(CO)_5PR_3$ complexes by another ligand causes the PR_3 chemical shift to be displaced upfield.[17,25] This has been rationalized as being due to steric interactions between ligands causing distortions of the bond angles around both the metal and phosphorus. Thus, as the sizes of the ligands L and L′ increase, the more shielded the ligand ^{31}P NMR chemical shifts in cis-$W(CO)_4(L)(L')$ complexes become. In general, our chemical shifts bear this out, as shown in Table III. In fact, there is reasonable agreement between chemical shifts and cis:trans ratios. The chemical shifts of $PPhMe_2$, PPh_2Et, and $P(p\text{-tol})_3$ in cis complexes with PEt_3 and $P(n\text{-}Bu)_3$, however, are inconsistent with those from the other complexes when PEt_3 and $P(n\text{-}Bu)_3$ are assigned 132° cone angles. A much better correlation would be obtained if they had cone angles comparable to or slightly larger than PPh_2Et (142°).[1] Again, the effect of PMe_3 is in line with the other ligands and not with PEt_3 and $P(n\text{-}Bu)_3$.

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Registry No. **1**, 97704-32-0; **2**, 97704-33-1; **3**, 97704-34-2; *cis*-**4**, 97704-35-3; *trans*-**4**, 97747-97-2; *cis*-**5**, 61347-94-2; *trans*-**5**, 24554-49-2; *cis*-**6**, 97704-36-4; *trans*-**6**, 97747-98-3; *cis*-**7**, 97704-37-5; *trans*-**7**, 97747-99-4; *cis*-**8**, 97704-38-6; *trans*-**8**, 97748-86-2; *cis*-**9**, 97704-39-7; *trans*-**9**, 97748-00-0; *cis*-**10**, 97704-40-0; *trans*-**10**, 97748-01-1; *cis*-**11**, 97704-41-1; *trans*-**11**, 97748-02-2; *cis*-**12**, 97704-42-2; *trans*-**12**, 97748-03-3; *cis*-**13**, 97704-43-3; *trans*-**13**, 97748-04-4; *cis*-**14**, 97704-44-4; *trans*-**14**, 97748-87-3; *cis*-**15**, 97704-45-5; *trans*-**15**, 97748-05-5; *cis*-**16**, 97748-85-1; *trans*-**16**, 97704-58-0; *cis*-**17**, 97704-46-6; *trans*-**17**, 97748-06-6; *cis*-**18**, 97704-47-7; *trans*-**18**, 97748-07-7; *cis*-**19**, 97747-96-1; *trans*-**19**, 32370-61-9; *cis*-**20**, 97704-48-8; *trans*-**20**, 97748-08-8; *cis*-**21**, 97704-49-9; *trans*-**21**, 97748-09-9; *cis*-**22**, 97704-50-2; *trans*-**22**, 97748-10-2; *cis*-**23**, 97704-51-3; *trans*-**23**, 97748-11-3; *cis*-**24**, 97704-52-4; *trans*-**24**, 97748-12-4; *cis*-**25**, 97704-53-5; *trans*-**25**, 97748-13-5; *cis*-**26**, 97704-54-6; *trans*-**26**, 97748-14-6; *cis*-**27**, 97704-55-7; *trans*-**27**, 97748-15-7; *cis*-**28**, 36491-17-5; *trans*-**28**, 36573-15-6; *cis*-**29**, 97704-56-8; *trans*-**29**, 97748-16-8; *cis*-**30**, 97704-57-9; *trans*-**30**, 97748-17-9; *cis*-**31**, 21246-26-4; *trans*-**31**, 21246-25-3; *cis*-**32**, 87301-05-1; *trans*-**32**, 97748-18-0; $W(CO)_4(py)_2$, 40903-14-8; PH_3, 7803-51-2.

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