Synthesis and Reactivity of $[(\eta^6\text{-Biphenylene})Mn(CO)_3]^+$

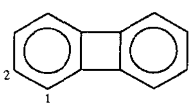
Conor A. Dullaghan, Gene B. Carpenter, and D. A. Sweigart*

Abstract: Biphenylene readily coordinates through one of the phenyl rings to form $[(\eta^6\text{-biphenylene})Mn(CO)_3]^+$ ($\mathbf{2}^+$), the X-ray structure of which is reported. The nucleophiles H^-, Me^-, $Me_3CC(O)CH_2^-$, and $P(OEt)_3$ add to $\mathbf{2}^+$ at a bridgehead carbon to afford high yields of cyclohexadienyl complexes (**3**); the X-ray structure of the product of hydride addition is reported. $P(OMe)_3$ adds to $\mathbf{2}^+$ to give **3**, which then undergoes a spontaneous Arbuzov elimination to the dimethyl phosphonate adduct. Nucleophilic additions to $\mathbf{2}^+$ are unusual in that they occur at a substituted (bridgehead) carbon. A kinetic and thermodynamic study of the reaction with $P(OEt)_3$ shows that the bridgehead carbons in $\mathbf{2}^+$ are orders of magnitude more electrophilic than are the arene carbons in unstrained $[(arene)Mn(CO)_3]^+$ systems.

Keywords
Arbuzov reactions · biphenylene · cyclohexadienyl complexes · manganese

Introduction

Biphenylene (**1**) is a thermally stable molecule that has been known for more than half a century.[1] Although it can be viewed as a substituted cyclobutadiene, the four-membered ring in **1** possesses little diene character and essentially none of the chemical reactivity normally associated with cyclobutadienes. Compound **1** undergoes electrophilic substitution predominately at C-2; the four-membered ring is fairly robust, but can be cleaved thermally at high temperatures or by catalytic hydrogenation.[1, 2] Organometallic complexes of **1** are known in which one or both of the phenyl rings are η^6-bonded to chromium[3, 4] or molybdenum.[5] It has been noted that chromium biphenylene sandwich complexes are inert to associative ligand substitution, whereas analogous chromium naphthalene complexes are quite reactive.[4] This marked contrast in behavior was ascribed to a greater ease of ring slippage from η^6 to η^4 with the naphthalene species. Other than this observation that biphenylene ligands are not readily displaced, there have been no reports concerning the chemical reactivity of biphenylene complexes. Herein we demonstrate that $Mn(CO)_3^+$ is readily coordinated to biphenylene to afford the thermally stable $[(\eta^6\text{-biphenylene})Mn(CO)_3]^+$ ($\mathbf{2}^+$). The coordinated phenyl ring in $\mathbf{2}^+$ is electrophilically activated and undergoes facile nucleophilic addition reactions with H, P, and C donors at a bridgehead carbon (C-11) to afford cyclohexadienyl complexes **3**.



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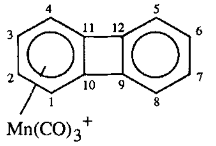
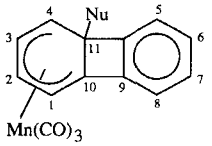


$\mathbf{2}^+$



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Results and Discussion

The synthesis of $[\mathbf{2}]BF_4$ was easily accomplished by a recently developed method that is based on the naphthalene substitution reaction in Equation (1).[6] The key to this synthetic route is

$$[(naphthalene)Mn(CO)_3]BF_4 \xrightarrow[CH_2Cl_2]{biphenylene} [(biphenylene)Mn(CO)_3]BF_4 \quad (1)$$

the ease with which the naphthalene ligand can slip from η^6 to η^4 bonding as the incoming biphenylene binds to the metal, affording a pathway for subsequent loss of the naphthalene and η^6-bonding of the biphenylene to the metal. In contrast to the behavior of manganese tricarbonyl complexes with naphthalene-type polyarene ligands, complex $\mathbf{2}^+$ was found to be unreactive to arene displacement by the donor solvents MeCN or Me_2CO. This indicates that the biphenylene ligand does not easily slip to η^4-bonding. In accordance with this conclusion, the electrochemical reduction of $\mathbf{2}^+$ in $CH_2Cl_2/0.10\,\text{M}\ Bu_4NPF_6$ is chemically irreversible at a scan rate of $0.50\,Vs^{-1}$ ($E_p = -0.66$ V relative to $E_{1/2} = 0.53$ V for ferrocene). Manganese arene complexes that readily slip to η^4-bonding, such as $[(naphthalene)Mn(CO)_3]^+$, are reduced in a chemically reversible two-electron step to give relatively stable anionic complexes.[7, 8]

The molecular structure of $\mathbf{2}^+$ is shown in Figure 1. The biphenylene part of the molecule is highly planar and the Mn–CO linkages are arranged in an "*endo*" conformation, meaning

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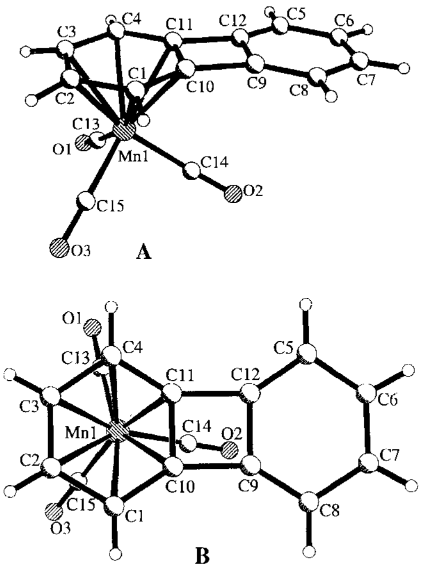

Fig. 1. Two views of $\mathbf{2}^+$. Selected bond lengths [Å]: C9–C10 1.497(6), C10–C11 1.433(5), C11–C12 1.514(5), C12–C9 1.412(6), Mn–C1 2.227(5), Mn–C2 2.156(4), Mn–C3 2.150(4), Mn–C4 2.234(4), Mn–C11 2.197(4), Mn–C10 2.220(4).

that one of the Mn–CO vectors points towards the interior of the biphenylene ligand, as shown in Figure 1 B. An analogous *endo* conformation was found for [(biphenylene)Cr(CO)$_3$], and rationalized on the basis of MO calculations.[3] By way of comparison, [(naphthalene)Cr(CO)$_3$] and other polyarene chromium tricarbonyl complexes have an "*exo*" structure, with none of the Cr–CO groups pointing towards the interior of the π-polyarene ligand.[9] An attempt was made to coordinate a second Mn(CO)$_3^+$ moiety to the uncomplexed phenyl ring in $\mathbf{2}^+$, but this proved to be unsuccessful, probably due to unfavorable electrostatics and a concomitant reduction in π-donor ability.

The reaction of $\mathbf{2}^+$ with nucleophilic reagents gave cyclohexadienyl complexes as expected. However, these reactions proved to be unusual in two ways. Normally, nucleophiles attack at an unsubstituted carbon in [(arene)Mn(CO)$_3$]$^+$ complexes, often with useful regioselectivity.[7] In contrast, addition to $\mathbf{2}^+$ occurs exclusively at a substituted (bridgehead) carbon. The nucleophiles H$^-$, Me$^-$, Me$_3$CC(O)CH$_2^-$, and P(OEt)$_3$ all reacted smoothly to give **3** in high yield. Reaction with P(OMe)$_3$ also gave **3**, which was observed to undergo within minutes a spontaneous Arbuzov elimination to afford the dimethyl phosphonate product (**3**, Nu = P(O)(OMe)$_2$). Analogous formation of dimethyl phosphonate adducts from reactions with P(OMe)$_3$ are well known with other π-hydrocarbon complexes.[10] The X-ray structure of **3** (Nu = H) is shown in Figure 2. In this molecule the dienyl carbons C1-C2-C3-C4-C10 are highly planar and the fold angle of the C4-C10-C11 plane about the dienyl plane is 44.8°. The most interesting structural change occurring upon hydride addition to $\mathbf{2}^+$ resides in the four-carbon ring C9–C12. Bonds C10–C11 and C11–C4 lengthen by more than 0.10 Å and atom C11 is pulled up and away from the dienyl plane; these changes are reflected in a significant decrease of 5° in the C10-C11-C12 bond angle.

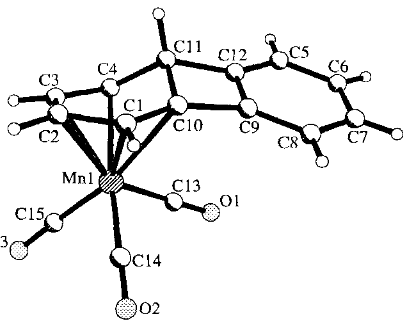

Fig. 2. X-ray structure of **3** (Nu = H). Selected bond lengths [Å]: C9–C10 1.478(4), C10–C11 1.536(4), C11–C12 1.530(4), C12–C9 1.390(4), C11–C4 1.502(4), Mn–C1 2.163(3), Mn–C2 2.128(3), Mn–C3 2.117(3), Mn–C4 2.216(3), Mn–C10 2.274(3).

The structural changes just noted suggest that a bridgehead carbon in $\mathbf{2}^+$ is attacked in preference to an unsubstituted position because of the relaxation of steric and electronic constraints inherent in the "cyclobutadiene" ring in biphenylene. This explanation also accounts for a second unusual aspect of nucleophilic addition to $\mathbf{2}^+$—the bridgehead carbons have an unexpectedly high electrophilicity. In a qualitative sense, $\mathbf{2}^+$ is judged to be more electrophilic than any other known [(arene)Mn(CO)$_3$]$^+$ complex. This follows from the observation that coordinated biphenylene is the only arene that reacts with P(OEt)$_3$ to form a cyclohexadienyl complex. IR spectra of mixtures of $\mathbf{2}^+$ and P(OEt)$_3$ allowed the equilibrium constant for Equation (2) to be determined as $K_{eq} = k_1/k_{-1} = 500 \pm 50\,\text{M}^{-1}$

$$[(\text{biphenylene})\text{Mn(CO)}_3]^+ + \text{P(OEt)}_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\text{biphenylene}\cdot\text{P(OEt)}_3)\text{Mn(CO)}_3]^+ \qquad (2)$$

at 25 °C in acetone. By comparison, K_{eq} for the addition of P(nBu)$_3$ to [(benzene)Mn(CO)$_3$]$^+$ at 25 °C is only 290 M^{-1}, even though P(nBu)$_3$ is a far stronger base than P(OEt)$_3$.[11] The kinetics of the reaction in Equation (2) was followed under pseudo first order conditions with P(OEt)$_3$ in excess. The observed rate constant was found to obey the predicted equation, $k_{obs} = k_1[\text{P(OEt)}_3] + k_{-1}$, with $k_1 = 2.3\,\text{M}^{-1}\text{s}^{-1}$ and $k_{-1} = 0.0046\,\text{s}^{-1}$, which gives the same equilibrium constant found with the static IR data.

It is interesting to inquire how much the electrophilicity of the bridgehead carbons in $\mathbf{2}^+$ exceeds that of the "unstrained" substituted arene carbons in, for example, [(p-xylene)Mn(CO)$_3$]$^+$ ($\mathbf{4}^+$). It is not possible to determine this experimentally, because nucleophiles attack only unsubstituted positions in manganese complexes with simple arenes such as p-xylene. However, a comparison of the reactivity of the *unsubstituted* arene carbons in $\mathbf{4}^+$ to that of the bridgehead carbons in $\mathbf{2}^+$ is possible. In this way, one can obtain a lower limit of the reactivity difference for addition to the respective *substituted* carbons (it is a lower limit because unsubstituted carbons are known to be more electrophilic than substituted ones in unstrained arene complexes).[12] The comparison to be made is for P(OEt)$_3$ addition to $\mathbf{2}^+$ and to $\mathbf{4}^+$, even though, for thermodynamic reasons, P(OEt)$_3$ does not add to $\mathbf{4}^+$! The basis for this depends on the well documented observation[12, 13] that the relative nucleophilic reactivity of P donors is independent of the electrophile for a wide range of organometallic π-hydrocarbon complexes as well as for free carbocations. Thus, for example, it is known that P(OEt)$_3$

is always less reactive than $P(nBu)_3$ by a factor of $10^{4.1}$. The rate of addition of $P(nBu)_3$ to 4^+ in acetone at 25 °C is known[11] to be $350\,M^{-1}s^{-1}$, from which one calculates that the rate of $P(OEt)_3$ addition to 4^+, if it were to occur, would be $0.03\,M^{-1}s^{-1}$. This means that the bridgehead carbons in 2^+ are about 75 times more electrophilic than are the unsubstituted carbons in 4^+; the differential would be even greater for the substituted carbons in 4^+.

Conclusion

The bridgehead carbon atoms in $[(\text{biphenylene})Mn(CO)_3]^+$ are extraordinarily electrophilic and readily undergo nucleophilic addition reactions to afford high yields of stable cyclohexadienyl complexes.

Experimental Procedure

All reactions were carried out under an atmosphere of dry nitrogen with standard Schlenk techniques, where applicable. Microanalyses were performed by National Chemical Consulting, Tenafly, NJ. HPLC grade CH_2Cl_2 was purchased from Fisher Scientific and was stored under N_2 over 4 Å molecular sieves. $AgBF_4$ and Mn_2CO_{10} were purchased from Strem Chemical Co. and stored in a nitrogen-filled glove bag between use. $Mn(CO)_5Br$ was prepared from Mn_2CO_{10} [14]. $[(\eta^6\text{-naphthalene})Mn(CO)_3]BF_4$ was prepared as recently reported [6]. Activated neutral alumina (Brockmann I, ca. 150 mesh, 58 Å) was deactivated by adding H_2O to form a 10%, w/w mixture. Electrochemical measurements were made as previously described [15].

$[(\eta^6\text{-Biphenylene})Mn(CO)_3]BF_4$ ([**2**]BF_4): Biphenylene (0.068 g, 0.45 mmol) was added to a solution of $[(\eta^6\text{-naphthalene})Mn(CO)_3]BF_4$ (0.152 g, 0.400 mmol) in CH_2Cl_2 (ca. 15 mL) under N_2. The mixture was sealed in a pressure bottle and heated to 70 °C for 2 h. The reaction mixture was then cooled to room temperature and concentrated in vacuo. The addition of Et_2O (ca. 40 mL) precipitated the product as a pale yellow powder, which was collected by filtration, washed with Et_2O and dried in vacuo. Yield 91%; IR (CH_2Cl_2): $\tilde{\nu}_{co}$ [cm^{-1}] = 2077 (s), 2022 (s, br); ^1H NMR (CD_2Cl_2): δ = 7.31 (m, $H^{5,6,7,8}$), 6.38 (m, $H^{1,2,3,4}$). Anal (%) calcd for $C_{15}H_8O_3MnBF_4$: C 47.62, H 2.12; found C 47.39, H 2.21.

A crystal of [**2**]BF_4 suitable for X-ray diffraction was grown by slow diffusion of degassed diethyl ether into an acetone solution at −20 °C. The crystal structure of [**2**]BF_4 was determined on a Siemens P4 diffractometer. Data collection was at 25 °C with $Mo_{K\alpha}$ radiation. No systematic decrease in the intensities of three standard reflections was observed. Intensities were extracted with profile fitting and a semiempirical absorption correction was applied. For [**2**]BF_4: monoclinic space group $P2_1/n$, a = 9.2187(14), b = 10.6735(10), c = 15.344(2) Å, β = 102.981(10)°, V = 1471.2(3) Å^3, Z = 4, ρ_{calcd} = 1.706 g cm^{-3}, μ = 0.954 mm^{-1}, θ range 2.34–30.00°, 232 variables refined with 4283 independent reflections to R = 0.0614, w$R2$ = 0.1362, GOF = 0.868. The structure was determined by direct methods and refined on F^2 with the programs in the SHELXTL PC version 5 package. All hydrogen atoms appeared in a difference map and each was placed in an ideal position, riding on the atom to which it is bonded; each was refined with an isotropic temperature factor 20% greater than that of the ridden atom. The tetrafluoroborate anion showed disorder and was modeled as two rigid tetrahedral groups, each with one-half occupancy. The boron atoms were constrained to have equal isotropic displacement parameters; the fluorine atoms were refined with anisotropic displacements.

Crystallographic data (excluding structure factors) for the structures reported in this paper {[**2**]BF_4 and **3** (Nu = H)} have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-38. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

$[(\eta^5\text{-Biphenylene}\cdot H)Mn(CO)_3]$ (**3**, Nu = H): The cyclohexadienyl complex **3** with Nu = H was synthesized as follows. Complex [**2**]BF_4 (0.038 g, 0.1 mmol) in CH_2Cl_2 (5 mL) under N_2 was treated with $[Bu_4N][BH_3CN]$ (0.040 g, 0.14 mmol), and the mixture was stirred at 0 °C for 10 min and then at room temperature for a further 10 min. The CH_2Cl_2 was removed in vacuo, and the residue taken up in Et_2O and chromatographed through a neutral Al_2O_3 column with hexanes as the eluent. The product crystallized from a concentrated hexanes solution at −20 °C. Yield 81%; IR (hexanes): $\tilde{\nu}_{co}$ [cm^{-1}] = 2029 (s), 1954 (s), 1936 (s); ^1H NMR (CD_2Cl_2): δ = 7.29 (m, $H^{6,7}$), 7.13 (m, $H^{5,8}$), 5.57 (t, J = 4.6 Hz, H^2), 5.15 (d, J = 6.9 Hz, H^1), 5.06 (t, J = 6.9 Hz, H^3), 4.09 (d, J = 6.9 Hz, H^4), 3.95 (s, H^{11}); Anal (%) calcd for $C_{15}H_9O_3Mn$: C 61.64, H 3.08; found C 61.59, H 3.16. Other nucleophilic addition products (**3**) were prepared by roughly similar procedures to that used for Nu = H, as briefly described below.

A crystal of **3** (Nu = H) suitable for X-ray diffraction was grown by slow evaporation from a degassed pentane solution at room temperature. The crystal structure was determined on a Siemens P4 diffractometer equipped with a CCD area detector and controlled by SMART version 4 software. Data collection was at 25 °C with $Mo_{K\alpha}$ radiation. Data reduction was carried out by SAINT version 4 software and included profile analysis, correction for a 6.6% intensity increase during data collection, and a laminar semiempirical absorption correction. For **3**: triclinic space group $P1$, a = 6.6090(2), b = 10.1280(2), c = 10.1570(2) Å, α = 65.794(1), β = 82.272(2), γ = 79.741(2)°, V = 608.77(2) Å^3, Z = 2, ρ_{calcd} = 1.594 g cm^{-3}, μ = 1.083 mm^{-1}, θ range 2.20–23.27°, 172 variables refined with 1588 independent reflections to R = 0.0386, w$R2$ = 0.1047, GOF = 1.105. The structure was determined by direct methods and refined on F^2 using the programs in the SHELXTL PC version 5 package. All hydrogen atoms appeared in a difference map and each was placed in an ideal position, riding on the atom to which it is bonded; each was refined with an isotropic temperature factor 20% greater than that of the ridden atom.

3 (Nu = Me): [**2**]BF_4 (0.038 g, 0.1 mmol) in CH_2Cl_2 (5 mL) at −78 °C was treated with 1.5 equiv of MeLi (THF) or MeMgBr (THF). The mixture was then warmed to room temperature over 30 min, and the solvent removed. The residue was extracted with hexanes and chromatographed as above to afford product in 72% yield. IR (hexanes): $\tilde{\nu}_{co}$ [cm^{-1}] = 2020 (s), 1954 (s), 1937 (s); ^1H NMR (CD_2Cl_2): δ = 7.18 (m, $H^{6,7}$), 7.07 (m, $H^{5,8}$), 5.49 (t, J = 4.7 Hz, H^2), 5.17 (d, J = 4.7 Hz, H^1), 5.00 (t, J = 6.5 Hz, H^3), 4.21 (d, J = 6.4 Hz, H^4), 1.14 (s, Me). Anal (%) calcd for $C_{16}H_{11}O_3Mn$: C 62.76, H 3.62; found C 63.06, H 3.83.

3 (Nu = CH_2COCMe_3): A solution of $LiCH_2COCMe_3$ was prepared by adding LDA to a THF solution of pinacolone at −78 °C. To a stirred suspension of [**2**]BF_4 (0.076g, 0.2 mmol) in Et_2O (10 mL) at −78 °C, $LiCH_2COCMe_3$ (1.5 equiv) was added dropwise over 2 min. The mixture was stirred for 4 min and then allowed to warm to room temperature. The solvent was removed in vacuo, and the residue extracted with Et_2O (4 mL) and chromatographed through Al_2O_3 with hexanes/Et_2O (2:1, v/v) as the eluent. The product crystallized from a concentrated pentane solution at −20 °C. Yield 83%; IR (hexanes): $\tilde{\nu}_{co}$ [cm^{-1}] = 2022 (s), 1956 (s), 1939 (s); ^1H NMR (CD_2Cl_2): δ = 7.26 (m, $H^{6,7}$), 7.05 (m, $H^{5,8}$), 5.52 (t, J = 5.5 Hz, H^2), 5.16 (d, J = 4.7 Hz, H^1), 4.94 (t, J = 4.8 Hz, H^3), 4.94 (d, J = 6.8 Hz, H^4), 2.65 (d, J = 18 Hz, CH_2), 2.34 (d, J = 18 Hz, CH_2), 1.03 (s, Me).

3 (Nu = $P(O)(OMe)_2$): An excess of $P(OMe)_3$ was added to [**2**]BF_4 (0.020 g, 0.053 mmol) in CH_2Cl_2 (10 mL). An immediate color change from pale yellow to a deep clear yellow was accompanied by a change in the IR spectrum of the solution to $\tilde{\nu}_{co}$ = 2029 (s), 1960 (s, br) cm^{-1}, which then changed over a period of a few minutes to 2018 (s), 1946 (s), 1935 (s) cm^{-1}. When this change was complete, the solution was concentrated, and the reaction mixture chromatographed through Al_2O_3 with acetone as the eluent. The product obtained was crystallized from pentane/Et_2O (5:1, v/v) at −20 °C. Yield 92%; IR (CH_2Cl_2): $\tilde{\nu}_{co}$ [cm^{-1}] = 2018 (s), 1946 (s), 1935 (s); ^1H NMR (CD_2Cl_2): δ = 7.36 (m, $H^{6,7}$), 7.15 (m, $H^{5,8}$), 5.39 (t, J = 5.0 Hz, H^2), 5.27 (m, $H^{1,3}$), 4.14 (d, J = 6.7 Hz, H^4), 3.55 (dd, J = 10.5 Hz, Me). Anal (%) calcd for $C_{17}H_{14}O_6PMn$: C 51.02, H 3.53; found C 50.88, H 3.55.

3 (Nu = $P(OEt)_3$): An excess of $P(OEt)_3$ was added to [**2**]BF_4 (0.020 g, 0.053 mmol) in CH_2Cl_2 (10 mL). This resulted in an immediate color change from a pale yellow to a deep yellow. After it had been stirred for 15 min, the reaction was concentrated, Et_2O (30 mL) was added, and the reaction mixture was placed in a refrigerator. Deep yellow needlelike crystals of the BF_4^- salt were obtained over a period of 3 d. Yield 79%; IR (CH_2Cl_2): $\tilde{\nu}_{co}$ [cm^{-1}] = 2029 (s), 1960 (s); ^1H NMR (CD_2Cl_2): $\delta = 7.40$ (m, $H^{5,6,7,8}$), 5.73 (t, $J = 4.9$ Hz, H^2), 5.55 (d, $J = 4.5$ Hz, H^1), 5.47 (t, $J = 6.5$ Hz, H^3), 4.14 (d, $J = 6.6$ Hz, H^4), 4.25 (m, CH_2), 1.35 (t, $J = 6.8$ Hz, Me).

Kinetic and Thermodynamic Studies: The kinetics of nucleophilic addition of $P(OEt)_3$ to [**2**]BF_4 was followed by the stopped-flow technique as described previously [11]. The solvent was HPLC grade acetone, and the temperature 25 °C. The reaction was monitored at 390 nm with [**2**]BF_4 present at 2.0×10^{-4} M and $P(OEt)_3$ in pseudo first order excess at either 0.015 or 0.0075 M. Standard plots of $\ln(A_\infty - A)$ vs. time, highly linear throughout the reaction, were used to determine k_{obs} values. The equilibrium constant for the addition reaction was determined from static IR measurements in the $\tilde{\nu}_{co}$ region, with the metal present at 0.0050 M and $P(OEt)_3$ at 0.0075 or 0.015 M.

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