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Synthesis of $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_2LPF_6$ and $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2L$ complexes (L = phosphines and phosphites) and kinetic studies of η^6 to η^5 ring slippage reactions

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Abstract

This report describes the syntheses and characterizations of $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_2LPF_6$ and $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2L$ complexes (L = $P(OEt)_3$, PPh_3, PEt_3, and η^1-(diphos) (diphos = 1,2-bis(diphenylphosphino)ethane), and kinetic studies of $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2L \rightarrow (\eta^5\text{-}C_{13}H_9)Mn(CO)_2L$ ring slippage reactions. $\Delta H^\ddagger$ values for the $\eta^6 \rightarrow \eta^5$ slippage reactions of the $P(OEt)_3$ (26.4 kcal/mol), PPh_3 (23.1 kcal mol^{-1}), and PEt_3 (25.6 kcal mol^{-1}) complexes are similar to values previously reported for CO and $P(n\text{-}Bu)_3$ complexes. The unusually low value of $\Delta H^\ddagger = 19.9$ kcal/mol for the η^1-diphos complex is attributed to an intermediate stabilized by an intramolecular nucleophilic attack of the free end of the diphos ligand on the metal center.

Key words: Manganese; Ring slippage; Kinetic studies; Phosphines; Phosphites

1. Introduction

Pentahapto indenyl (C_9H_7) and fluorenyl ($C_{13}H_9$) transition metal complexes have attracted chemists' attention because of their high reactivity compared to analogous η^5-cyclopentadienyl complexes. Less well studied are complexes in which a transition metal is bound to the six-membered ring of indenyl, indene, fluorenyl, or fluorene ligands [1-7]. There are several reports of reactions of $\eta^5\text{-}C_9H_7$ and $\eta^5\text{-}C_{13}H_9$ complexes with acids resulting in formation of $\eta^6\text{-}C_9H_8$ and $\eta^6\text{-}C_{13}H_{10}$ complexes in which the metal had slipped to the ligand's six-membered ring [1(a), 2(a),(e),(h),3,5]. Subsequent deprotonation of the $\eta^6\text{-}C_{13}H_{10}$ complexes yielded corresponding $\eta^6\text{-}C_{13}H_9$ complexes, normally followed by relatively slow slippage of the metal to the five-membered ring of the ligand; deprotonation of $\eta^6\text{-}C_9H_8$ complexes yielded $\eta^5\text{-}C_9H_7$ products, presumably via an unobserved, short-lived $\eta^6\text{-}C_9H_7$ intermediate. Similar reactions have also been observed for the reactions of indenyl and fluorenyl complexes with other electrophiles. Only a few $\eta^6\text{-}C_9H_7$ and $\eta^6\text{-}C_{13}H_9$ complexes have been isolated [2(c),(f)].

Because the reaction of pentahapto indenyl and fluorenyl complexes with electrophiles may cause slippage to the six-membered ring, factors influencing the rates of η^6-η^5 interchange should be of interest. However, few experimental studies comparing the relative stability of hexahapto with pentahapto coordination for indenyl and fluorenyl ligands have been described. Basolo [5] reported that the rates and activation parameters for the $\eta^6 \rightarrow \eta^5$ slippage of $(\eta\text{-}C_{13}H_9)Mn(CO)_2L$ (L = CO, $P(n\text{-}Bu)_3$) were very similar and concluded that electronic factors had little effect. In contrast, Ceccon [4(b)] studied the anionic complexes $(\eta\text{-}C_{13}H_9)Cr(CO)_2L^-$ (L = CO, $P(OPh)_3$, PPh_3, and $P(n\text{-}Bu)_3$) and observed a strong electronic influence on both the position of the $\eta^6 \rightleftharpoons \eta^5$ equilibrium and the rate of $\eta^6 \rightarrow \eta^5$ slippage. Computational studies [8] have suggested that inter-ring slippage reactions proceed via exocyclic transition states rather than via least-motion trajectories, but to our knowledge, com-

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putational studies have not addressed the influence of electronic factors on the activation barriers of such reactions.

Our own interest in the reactivity of η^6-fluorenyl complexes was spurred, in part, by our observation that both $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$ (**Ia**) and $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ (**IIIa**) react with alkylphosphines, PR_3 (R = ethyl and n-butyl), to yield the same monohapto fluorenyl product, $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PR_3)_2$, and that the reaction proceeds much more rapidly for $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$, in spite of the fact that the reaction requires the fluorenyl moiety to slip from its six-membered ring to its five-membered ring [9]. This observation demonstrates the higher reactivity of η^6-fluorenyl complexes, and suggests further investigation of their chemistry. In this study, we have sought to investigate synthetic routes to η^6-fluorenyl compounds and to extend the kinetic studies on $\eta^6 \to \eta^5$ slippage reported by Basolo.

2. Results and discussion

2.1. Synthetic studies

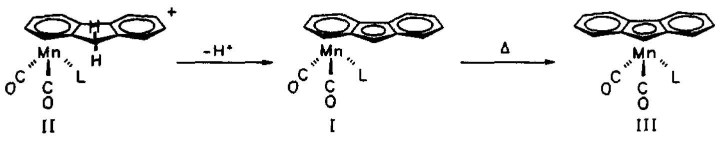
$(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ (**IIIa**) and some of its derivatives were first reported by King and Efraty, 1970 [10]. Prior to this work, the only $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2L$ (**I**) and $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_2L^+$ (**II**) complexes reported were those for which L = CO (**Ia** and **IIa**) [1(d)] and L = $P(n\text{-}Bu)_3$ [5]. Most of the syntheses described below employed as a starting material $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_3PF_6$ (**IIa**) which is readily prepared by the method of Treichel and Johnson [1(d)]. We have prepared a series of complexes for which L = $P(OEt)_3$ (**Ib** and **IIb**), PPh_3 (**Ic** and **IIc**), PEt_3 (**Id** and **IId**), and η^1-diphos (diphos = 1,2-bis(diphenylphosphino)ethane) (**Ie** and **IIe**). The syntheses of the new η^6-fluorenyl complexes (**Ib–Ie**) involved deprotonation of the corresponding η^6-fluorene complexes (**IIb–IIe**) by KO(t-Bu) in THF. Each of the η^6-fluorenyl complexes slips to its corresponding η^5-fluorenyl isomer, $(\eta^5\text{-}C_{13}H_9)Mn(CO)_2L$ (**IIIa–IIIe**), upon heating in solution. The key transformations are shown in the Scheme below.

IIb, **IIc**, and **IIe** were synthesized directly from **IIa**. Three general methods were evaluated, all of which produced the desired products in reasonable yields. The simplest method involved refluxing an acetone solution of **IIa** with an excess of the desired ligand. Reactions were typically complete in less than one hour. Detailed mechanistic studies were not carried out, but it appeared that both photochemical and thermal pathways were operative: products were formed even when the reaction mixtures were thoroughly shielded from light, but the reactions proceeded more rapidly when exposed to room lights. Reaction mixtures that had been degassed but not heated yielded products slowly when exposed to room lights.

Since **IIa** is formally analogous to $(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$, methods described by Sweigart [11] for preparing $(\eta^6\text{-arene})Mn(CO)_2L^+$ (L = phosphorus ligand) complexes were also investigated. Photolysis of acetone solutions of **IIa** with excess ligand proved efficient; the reactions could be driven by indirect sunlight or room light, but photolysis with medium pressure mercury lamps generally led to decomposition and low yields. Substitution reactions employing trimethylamine-N-oxide were also evaluated. A complication of this synthetic strategy is that trimethylamine, a product of the reaction, is sufficiently basic to deprotonate **IIa**. This side reaction could be suppressed by adding acid to the reaction mixture, but because of the extra complications required for product isolation, this route was found to be the least favorable of the three methods evaluated.

IId could not be prepared directly from **IIa** using any of the methods described above because PEt_3 is sufficiently basic to deprotonate **IIa**. Therefore, **IId** was prepared using a procedure similar to that employed by Basolo [5] to synthesize the corresponding $P(n\text{-}Bu)_3$ complex: $(\eta^5\text{-}C_{13}H_9)Mn(CO)_2PEt_3$ (**IId**), prepared photochemically from $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ and PEt_3, was protonated with HCl; metathesis with aqueous NH_4PF_6 yielded **IId**.

Examples of each of the preparative methods described above are given in the Experimental section. All of the fluorene complexes, **II**, were yellow solids which appeared to be relatively air-stable. ^1H NMR spectra of **IIb–IIe** were similar to that reported by Treichel [1(d)] for **IIa**, showing peaks corresponding to the fluorene ligands' uncomplexed six-membered ring (approximately 8.1–7.5 ppm), complexed six-member



a: L = CO
b: L = P(OEt)$_3$
c: L = PPh$_3$
d: L = PEt$_3$
e: L = η^1-diphos

ring (approximately 7.2–6.0 ppm), and five-membered ring (AB pattern centered between 4.4 and 4.2 ppm); peaks corresponding to the phosphorus ligand were also observed. For **Ie**, two distinct resonances were observed for the methylene groups of the diphos, consistent with its characterization as a η^1-diphos complex. The carbonyl stretching frequency of the IR spectra showed the two-band pattern expected for **II**, with ν_{CO} decreasing in the order L = $P(OEt)_3 > PPh_3 > \eta^1$-diphos > PEt_3.

The fluorene complexes were readily deprotonated by KO(t-Bu) in THF to produce corresponding η^6-fluorenyl complexes, **I**, which were isolated as deep red to orange-red solids. ^1H NMR spectra of **Ib**–**Ie** showed peaks corresponding to the fluorenyl ligands' uncomplexed six-membered ring (8.1–7.2 ppm), complexed six-membered ring (6.5–4.3 ppm), and five-membered ring (approximately 6.0 ppm), again consistent with Treichel's [1(d)] observations for **Ia**. NMR spectra also indicated residual traces of solvent (hexane) even after prolonged evacuation; the crystal structure reported by Treichel [1(c)] for **Ia** included hexane. IR spectra (ν_{CO}) showed shifts to lower frequencies (40–50 cm^{-1}) compared with corresponding protonated species.

The ^1H NMR spectra of **Ie** was difficult to obtain in C_6D_6 because of the relatively high rate of its $\eta^6 \rightarrow \eta^5$ slippage reaction (see below) leading to formation of **IIIe**. The methylene protons of the η^1-diphos ligand appeared as a complex set of bands overlapped significantly by corresponding bands from **IIIe**. In both **Ie** and **IIe**, the four methylene protons of the η^1-diphos are magnetically inequivalent, and each may couple to both P atoms, so a relatively complex NMR pattern for these protons is not unexpected; however, the methylene peaks for **Ie** are distinctly broader than those of **IIe**. A potential source of additional broadening is interchange between the free and metal-bound ends of the η^1-diphos ligand via a transient species in which the diphos is bound as a chelate. Variable temperature (−50 to +10°C) ^1H NMR studies of **Ie** in $CDCl_3$ showed a temperature-dependent pattern in the 2–1 ppm region, with suggestion of peak broadening at higher temperatures. However, because of the conversion of **Ie** to **IIIe** at higher temperatures, and because of overlap of residual solvent peaks, a detailed analysis was not possible.

TABLE 1. First order rate constants for the reaction: $(\eta^6\text{-}C_{13}H_9)\text{-}Mn(CO)_2L \rightarrow (\eta^5\text{-}C_{13}H_9)Mn(CO)_2L$

	L	T(°C)	$k(s^{-1})$
Ia	CO	35.4	6.61×10^{-5}
		45.3	1.29×10^{-4}
		54.7	4.31×10^{-4}
		63.2	1.12×10^{-3}
Ib	$P(OEt)_3$	40.9	2.10×10^{-5}
		48.5	6.20×10^{-5}
		56.7	1.73×10^{-4}
		56.9	1.74×10^{-4}
		62.4	3.63×10^{-4}
		64.1	4.04×10^{-4}
Ic	PPh_3	43.3	9.11×10^{-5}
		43.8	9.76×10^{-5}
		50.2	2.09×10^{-4}
		54.6	3.54×10^{-4}
		58.9	5.32×10^{-4}
		63.3	8.69×10^{-4}
Id	PEt_3	39.8	1.18×10^{-4}
		48.6	4.06×10^{-4}
		59.4	1.44×10^{-3}
Ie	η^1-diphos	32.2	4.27×10^{-4}
		40.8	1.08×10^{-3}
		49.8	2.70×10^{-3}

TABLE 2. Activation parameters [a] for the reaction: $(\eta^6\text{-}C_{13}H_9)\text{-}Mn(CO)_2L \rightarrow (\eta^5\text{-}C_{13}H_9)Mn(CO)_2L$

	L	θ(°) [b]	$\Delta H^\ddagger$ (kcal mol^{-1}) [c]	$\Delta S^\ddagger$ (eu) [c]
Ia	CO	95	25.0±0.6	2.7±1.8
	CO [d]		25.2±0.1 [d]	2.3±0.4 [d]
Ib	$P(OEt)_3$	109	26.4±0.4	4.2±1.3
Ic	PPh_3	145	23.1±0.3	−4.0±0.9
Id	PEt_3	132	25.6±0.9	5.3±2.7
	PBu_3 [d]	132	24.2±1.4 [d]	−0.3±3.6 [d]
Ie	η^1-diphos	≈140 [e]	19.9±0.01	−8.8±0.02

[a] Isooctane solvent unless otherwise indicated.

[b] Tolman [13].

[c] Uncertainties reported for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are standard deviations, based on the standards deviations of the slopes and intercepts, respectively, of the regression lines.

[d] Hexane solvent, Rerek and Basolo [5].

[e] The value $\theta = 125$ given for diphos by Tolman [13] is half of the value for diphos as a chelate. The value listed above is that reported for $PEtPh_2$, which we believe represents a more realistic value for a singly-bound η^1-diphos ligand.

2.2. *Kinetic studies*

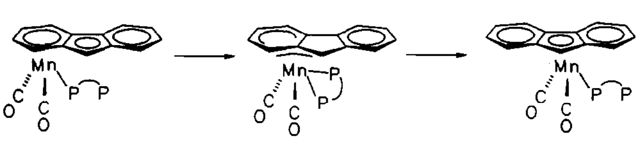
Rates and activation parameters were determined for the $\eta^6 \rightarrow \eta^5$ slippage reactions **I** → **III** in isooctane solvent. No attempt was made to isolate the η^5-fluorenyl products, **III**, but in each case, infrared spectra (ν_{CO}) of the products were consistent with those reported by Basolo for similar complexes [12].

Reactions were monitored in a temperature-controlled solution IR cell. Plots of $\ln(A_t\text{-}A_\infty$ *vs.* time were linear ($r^2 > 0.999$) for at least three half-lives, consistent with first-order kinetics. Rates were determined for at least three temperatures for each complex (Table 1), allowing determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (Table 2). Basolo's results for the $\eta^6 \rightarrow \eta^5$ slippage of $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$ and $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2P(n\text{-}$

Bu)$_3$ (in n-hexane solvent) [5] are also included in Table 2.

Our results for complexes **Ia–Id** support Basolo's contention [5] that electronic effects are of minimal importance in determining the activation enthalpies for $\eta^6 \rightarrow \eta^5$ slippage for the neutral manganese fluorenyl complexes considered here. Values of $\Delta H^\ddagger$ fall within a fairly narrow range (23.1 to 26.4 kcal mol^{-1}, average 25.0 kcal mol^{-1}) with no clear dependence on either the electronic (as judged by variation in ν_{CO}) or steric characteristics (cone angles, [13]) of L. The small values of $\Delta S^\ddagger$ are consistent with intramolecular processes.

Only the η^1-diphos complex (**Ie**) shows unusual behavior: its activation enthalpy ($\Delta H^\ddagger = 19.9$ kcal mol^{-1} is distinctly lower than that of the other complexes, a result which cannot be readily attributed to electronic or steric factors. A potential explanation for the higher reactivity of the η^1-diphos complex is suggested by computational studies [8] which indicate that ring slippage reactions occur via an exocyclic transition state which may, in this case, be viewed as a coordinately unsaturated η^3-fluorenyl species. We propose that the free end of the η^1-diphos ligand is capable of engaging in an intramolecular nucleophilic attack at the metal center, producing a stabilized intermediate in which the diphos is bound as a chelate.



The apparent broadening of the η^1-diphos methylene proton ^{1}H NMR signals is consistent with this model. We previously reported that low concentrations of PEt$_3$ catalyzed the $\eta^6 \rightarrow \eta^5$ slippage of **Ia** to **IIIa** [9]. Our new results further support the notion that ring-slippage reactions may be facilitated by nucleophiles.

3. Experimental section

Dry, oxygen-free solvents were used for all work. Synthetic reactions were carried out under nitrogen using Schlenk and cannula techniques; weighings and similar manipulations were carried out in a nitrogen-filled glove box. IR spectra were collected on a Nicolet/IBM IR44 FTIR spectrophotometer, and ^{1}H NMR were collected on a Varian Gemini 200 spectrometer operating at 200 MHz. (η^6-$C_{13}H_{10}$)Mn(CO)$_3$PF$_6$, (η^6-$C_{13}H_9$)Mn(CO)$_3$, and (η^5-$C_{13}H_9$)Mn(CO)$_3$ were prepared as described by Treichel and Johnson [1(d)]. PEt$_3$ and P(OEt)$_3$ (Aldrich) were distilled prior to use. PPh$_3$ (Baker), NH$_4$PF$_6$ (Strem), KO(t-Bu) (Aldrich), $(CH_3)_3NO \cdot 2H_2O$ (Aldrich), and CF$_3$CO$_2$H (Eastman) were used as received. Diphos (Strem) was recrystallized from hexane prior to use. Elemental analyses were carried out by Atlantic Microlab, Inc. (Norcross, GA).

The η^6-fluorene complexes (**II**) appeared to be air-stable, but were handled and stored under nitrogen as a general precaution. The η^6-fluorenyl complexes (**I**) were stored in a freezer (*ca.* −20°C) in a nitrogen-filled drybox until needed.

*3.1. (η^6-$C_{13}H_{10}$)Mn(CO)$_2$P(OEt)$_3$PF$_6$ (**IIb**)*

In a typical experiment, 0.318 g (0.707 mmol) **IIa** was combined with 5.0 g (30 mmol) P(OEt)$_3$ and 25 ml acetone. After three freeze–pump–thaw cycles, the reaction was left exposed to room lights for 3 h, at which time IR spectra showed complete conversion of **IIa** to **IIb**. The solvent was removed under vacuum, and the product washed with three small portions of hexane to remove excess P(OEt)$_3$. The product was recrystallized from acetone and ether to produce 0.288 g (69% yield) of bright yellow crystals. ^{1}H NMR (acetone-d_6) δ: 8.14 (1H, d, 7.1 Hz), 7.78 (1H, d, 7.0 Hz), 7.7–7.5 (2H, overlapping multiplets), 7.22 (1H, d, 5.2 Hz), 7.05 (1H, d, 5.5 Hz), 6.6–6.5 (2H, overlapping multiplets), 4.35 (2H, AB ($J = 22.7$ Hz, $\Delta\nu = 28.3$ Hz)), 4.10 (6H, p, $J_{HH} \approx J_{PH} = 6.9$ Hz), 1.30 (9H, t, 77.0 Hz). IR ν_{CO} (acetone): 2008, 1962 cm^{-1}. Analysis. calcd. for $C_{21}H_{25}F_6MnO_5P_2$: C, 42.9; H, 4.28. Found: C, 42.9; H, 4.26%.

*3.2 (η^6-$C_{13}H_9$)Mn(CO)$_2$P(OEt)$_3$ (**Ib**)*

In a typical experiment, 0.226 g (0.384 mmol) **IIb** and 43.1 mg (0.384 mmol) KO(^{t}-Bu) were combined with 10 ml THF, producing a deeply colored solution. After ten minutes, the THF solvent was removed under a stream of N$_2$. The product was extracted from the solid with three 2–3 ml portions of ether, which were transferred by cannula filter to another flask. The ether extracts were reduced to a volume of 1.5 ml under a stream of N$_2$, and then 8 ml hexane was added. The mixture was cooled to −78°C for 2 h resulting in precipitation of a red solid. The solvent was removed, leaving 80 mg (47% yield) of red solid product. ^{1}H NMR (benzene-d_6) δ: 8.03 (1H, d, 7.4 Hz), 7.83 (1H, d, 8.2 Hz), 7.51 (1H, t, 7.4 Hz), 7.21 (1H, t, 7.4 Hz), 6.46 (1H, dd, $J_{HH} = 6.2$ Hz, and $J_{PH} = 2.6$ Hz), 6.18 (1H, s), 5.82 (1H, d, 7.5 Hz), 4.78 (1H, t, 6.4 Hz), 4.40 (1H, t, 5.8 Hz), 3.35 (6H, p, $J_{HH} \approx J_{PH} = 6.9$ Hz), 0.87 (9H, t, 7.1 Hz). IR ν_{CO} (isooctane): 1970, 1913 cm^{-1}.

3.3. $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_2PPh_3PF_6$ (IIc)

In a typical experiment, 0.410 g (0.911 mmol) **IIa** (0.91 mmol), 107 mg (0.96 mmol) $(CH_3)_3NO \cdot 2H_2O$ and 2.4 g (9.1 mmol) PPh_3 were combined and dissolved in a mixture of 25 ml CH_2Cl_2 and 0.16 g (1.4 mmol) CF_3CO_2H. The mixture was stirred for 15 min at room temperature, extracted three times with deionized water to remove the CF_3CO_2H, and then dried with $MgSO_4$. Addition of hexane to the CH_2Cl_2 solution led to precipitation of a yellow solid. Excess PPh_3 was removed by extracting the solid repeatedly with hexane to produce 0.473 g (76% yield) of product. ^1H NMR (acetone-d_6) δ: 8.07 (1H, d, 6.6 Hz), 7.80 (1H, d, 7.0 Hz), 7.7–7.2 (17H, overlapping multiplets), 6.88 (2H, overlapping doublets), 6.28 (1H, m), 5.93 (1H, m), 4.37 (2H, AB ($J = 23.0$ Hz, $\Delta\nu = 33.6$ Hz)). IR ν_{CO} (acetone): 1997, 1952 cm^{-1}. Analysis: calcd. for $C_{33}H_{25}F_6MnO_2P_2$: C, 57.9; H, 3.68. Found: C, 58.3; H, 3.82%.

3.4. $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2PPh_3$ (Ic)

Ic was prepared using the same procedure as for **Ib**. Yield: 51%. ^1H NMR (benzene-d_6) δ: 7.92 (1H, d, 7.6 Hz), 7.81 (1H, d, 7.9 Hz), 7.57 (1H, t, 7.5 Hz), 7.27 (1H, t, 7.2 Hz), 7.2–7.1 (overlapping multiplets partially obscured by solvent peak), 7.0–6.8 (9H, overlapping multiplets), 6.13 (1H, d, 6.2 Hz), 5.92 (1H, s), 5.17 (1H, d, 7.4 Hz), 4.78 (1H, t, 6.4 Hz), 4.29 (1H, t, 5.9 Hz). IR ν_{CO} (isooctane): 1958, 1903 cm^{-1}.

3.5. $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_2PEt_3PF_6$ (IId)

$(\eta^5\text{-}C_{13}H_9)Mn(CO)_2PEt_3$ (**IId**) was prepared photochemically in 29% yield from **IIIa** and PEt_3 using a procedure analogous to that used by Basolo [5] to prepare the $P(n\text{-}Bu)_3$ complex. When HCl(g) was bubbled through a solution of **IIId** (0.076 g, 0.19 mmol) in 5 ml acetone, the color of the solution changed from orange to yellow. An aqueous solution of NH_4PF_6 (1.0 g, 6.1 mmol) was added, leading to partial precipitation of **IId**. The water–acetone mixture was removed under vacuum and the product extracted with CH_2Cl_2 and isolated by solvent removal. The product was recrystallized from acetone and ether to yield 0.045 g **IId** (43% yield). ^1H NMR (acetone-d_6) δ: 8.15 (1H, d, 6.3 Hz), 7.80 (1H, d, 6.3 Hz), 7.7–7.5 (2H, overlapping multiplets), 7.23 (1H, m), 7.02 (1H, m), 6.47 (2H, m), 4.38 (2H, AB ($J = 23.0$ Hz, $\Delta\nu = 32.6$ Hz), 2.00 (6H, m, partially obscured by solvent peaks), 1.09 (9H, dt, $J_{HH} = 7.5$ Hz, $J_{PH} = 16.6$ Hz). IR-ν_{CO} (acetone): 1989, 1943 cm^{-1}. Analysis: calcd. for $C_{21}H_{25}F_6MnO_2P_2$: C, 46.7; H, 4.66. Found: C, 43.1; H, 5.08%.

3.6. $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2PEt_3$ (Id)

Id was prepared in the same manner as **Ib**. Yield: 36%. ^1H NMR (benzene-d_6) δ: 7.93 (1H, d, 7.7 Hz), 7.75 (1H, d, 8.0 Hz), 7.53 (1H, t, 8.0 Hz), 7.23 (1H, partially obscured by solvent peak), 6.41 (1H, d, 6.0 Hz), 5.86 (1H, d, 2.0 Hz), 5.25 (1H, d, 7.1 Hz), 4.90 (1H, t, 6.6 Hz), 4.23 (1H, t, 6.3 Hz), 0.98 (6H, dq, $J_{HH} = 7.8$ Hz, $J_{PH} = 20$ Hz), 0.44 (9H, dt, $J_{HH} = 7.6$ Hz, $J_{PH} = 15.2$ Hz). IR ν_{CO} (isooctane): 1952, 1894 cm^{-1}.

3.7. $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_2(\eta^1\text{-}diphos)PF_6$ (IIe)

A solution of 0.513 g (1.14 mmol) **IIa** was added to a refluxing solution of 4.5 g (11.3 mmol) diphos in 60 ml acetone and heated for 45 min. The mixture was cooled on ice, precipitating a large portion of the excess diphos, and then filtered. Solvent was removed under vacuum, and the excess diphos removed by extraction, first with hexane, and then with hexane–benzene mixtures (4:1 to 1:1 v/v) until TLC of the extracts no longer showed evidence of diphos. The remaining solid was washed with hexane and then dried under vacuum, yielding 0.596 g (64% yield) **IIe**. ^1H NMR (acetone-d_6) δ: 7.85 (1H, d, 7.2 Hz), 7.74 (1H, d, 7.0 Hz), 7.7–7.1 (22H, overlapping multiplets), 6.87 (1H, dd, $J_{HH} = 6.3$ Hz, $J_{PH} = 2.1$ Hz), 6.79 (1H, d, 6.4 Hz), 6.21 (1H, t, 7.0 Hz), 5.91 (1H, dt, $J_{HH} = 7.0$ Hz, $J_{PH} = 2.8$ Hz), 4.21 (2H, AB ($J = 23.0$, $\Delta\nu = 59.1$ Hz). IR ν_{CO} (acetone): 1993, 1948 cm^{-1}. Analysis: calcd. for $C_{41}H_{34}F_6MnO_2P_3$: C, 60.0; H, 4.18. Found: C, 60.1; H, 4.25%.

3.8. $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2(\eta^1\text{-}diphos)$ (Ie)

Two milliliters of THF was added to a mixture of 137 mg **IIe** (0.167 mmol) and 22 mg KO(t-Bu) (0.20 mmol) held at −78°C. After 45 min, 8 ml hexane was added, and the solution filtered while cold. The solvent was removed under vacuum as the reaction mixture was slowly warmed to room temperature. An additional 5 ml hexane was added to partially redissolve the product, and then the hexane was removed under vacuum. (The purpose of the last step was to help remove entrapped THF). The product (35 mg) was found by ^1H NMR to contain small amounts of free diphos, **IIIe**, and fluorene. ^1H NMR (C_6D_6) δ: 7.97 (1H, d, 7.7 Hz), 7.85 (1H, d, 8.0 Hz), 7.56 (1H, t, 7.5 Hz), 7.25 (1H, t, 7.3 Hz), 7.3–6.8 (overlapping multiplets and solvent), 6.26 (1H, d, 6.2 Hz), 5.94 (1H, s), 4.8–4.6 (overlapping multiplets, 2H), 4.12 (1H, t, 5.5 Hz), 2.2–1.3 (complex set of multiplets). ^1H NMR spectrum of **Ie** recorded between −50°C and −10°C in $CDCl_3$ showed a similar pattern, with two complex bands (relative intensity of two each) centered at approximately 1.7 and 1.3 ppm. IR ν_{CO} (isooctane): 1952, 1896 cm^{-1}.

3.9. Kinetic studies

The variable-temperature IR solution cell employed for the kinetics measurements was locally built. The apparatus consisted of a CaF_2 or NaCl cavity cell (0.5

or 1.0 mm pathlength) mounted in a copper block through which temperature-regulated water flowed. A brass plate fitted with a small valve and thermocouple well served as the cover for the cell, with an o-ring used to provide a seal between the cover and cavity cell. Temperatures were monitored using a type K thermocouple connected to a Fluke 52 meter. Temperatures were controlled to ±0.1°C.

Dilute solutions of **II** (*ca.* 10^{-3} M) in isooctane were injected into the N_2-purged cavity cell and spectra recorded at appropriate time intervals. IR data for products (ν_{CO}): **IIIb** 1950, 1890 cm^{-1}; **IIIc** 1944, 1887 cm^{-1}; **IIId** 1937, 1875 cm^{-1}; **IIIe** 1938, 1878 cm^{-1}.

Rate constants were calculated from linear regressions of $\ln(A(t)-A_\infty)$ *vs.* time for each of the two absorbance peaks of **II**; A_∞ was treated as a variable parameter adjusted to optimize the regression.

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References

1 (a) P.M. Treichel and J.W. Johnson, *J. Organomet. Chem., 88* (1975) 207; (b) J.W. Johnson and P.M. Treichel, *J. Chem. Soc., Chem. Commun.*, (1976) 688; (c) J.W. Johnson and P.M. Treichel, *J. Am. Chem. Soc., 99* (1977) 1427; (d) P.M. Treichel and J.W. Johnson, *Inorg. Chem., 16* (1977) 749; (e) P.M. Treichel, K.P. Fivizzani and K.J. Haller, *Organometallics, 1* (1982) 931.

2 (a) A.N. Nesmeyanov, N.A. Ustynyuk, L.B. Makarova, S. Andre, Yu. A. Ustynyuk, L.N. Novikova and Yu.N. Luzikov, *J. Organomet. Chem., 154* (1978) 45; (b) N.A. Ustynyuk, B.V. Lokshin, Yu.F. Oprunenko, V.A. Roznyatovsky, Yu.N. Luzikov and Yu.A. Ustynyuk, *J. Organomet. Chem., 202* (1980) 279; (c) A.N. Nesmeyanov, N.A. Ustynyuk, L.N. Novikova, V.G. Andrianov, Yu.T. Struchkov, Yu.A. Ustynyuk, Yu.F. Oprunenko and Yu.N. Luzikov, *J. Organomet. Chem., 226* (1982) 239; (d) Yu.F. Oprunenko, Yu.N. Luzikov, Yu.A. Ustynyuk and N.A. Ustynyuk, *J. Organomet. Chem., 231* (1982) 137; (e) M.G. Yezernitskaya, B.V. Lokshin, V.I. Zdanovich, I.A. Lobanova and N.E. Kolobova, *J. Organomet. Chem., 234* (1982) 329; (f) A.N. Nesmeyanov, N.A. Ustynyuk, L.N. Novikova, T.N. Rybina, Yu.A. Ustynyuk, Yu.F. Oprunenko and O.I. Trifonova, *J. Organomet. Chem., 184* (1982) 63; (g) N.A. Ustynyuk, Yu.F. Oprunenko, S.G. Malyugina, O.I. Trifonova and Yu. A. Ustynyuk, *J. Organomet. Chem., 270* (1984) 185; (h) M.G. Yezernitskaya, B.V. Lokshin, V.I. Zdanovich, I.A. Lobanova and N.E. Kolobova, *J. Organomet. Chem., 282* (1985) 363; (i) L.N. Novikova, N.A. Ustynyuk, V.E. Zvorykin, L.S. Dneprovskaya and Yu. A. Ustynyuk, *J. Organomet. Chem., 292* (1985) 237.

3 C. White, S.J. Thompson and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1976) 409.

4 (a) A. Ceccon, A. Gambaro, G. Agostini and A. Venzo, *J. Organomet. Chem., 217* (1981) 79; (b) A. Ceccon, A. Gambaro, A. Venzo, V. Lucchini, T.E. Bitterworf and J. Shade, *J. Organomet. Chem., 327* (1987) 55.

5 M.E. Rerek and F. Basolo, *Organometallics, 3* (1984) 647.

6 A. Fessenbecker, M. Stephan, R.N. Grimes, H. Pritzkow, U. Zenneck and W. Siebert, *J. Am. Chem. Soc., 113* (1991) 3061.

7 (a) M.L.H. Green, N.G. Lowe and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, (1986) 1547; (b) M.L.H. Green, N.G. Lowe and D. O'Hare, *J. Organomet. Chem., 355* (1988) 315.

8 (a) T.A. Albright, P. Hofmann, R. Hoffmann, C.P. Lillya and P.A. Dobosh, *J. Am. Chem. Soc., 105* (1983) 3396; (b) K. Nakasuji, M. Yamaguchi, I. Murata, K. Tatsumi and A. Nakamura, *Organometallics, 3* (1984) 1257; (c) J. Silvestre and T.A. Albright, *J. Am. Chem. Soc., 107* (1985) 6829.

9 R.N. Biagioni, I.M. Lorkovic, J. Skelton and J.B. Hartung, *Organometallics, 9* (1990) 547.

10 R.B. King and A. Efraty, *J. Organomet. Chem., 23* (1970) 527.

11 (a) L.A.P. Kane-Maguire and D.A. Sweigart, *Inorg. Chem., 18* (1979) 700; (b) W.A. Halpin, J.C. Williams, T. Hanna and D.A. Sweigart, *J. Am. Chem. Soc., 111* (1989) 376.

12 M.E. Rerek and F. Basolo, *Organometallics, 3* (1984) 740.

13 C.A. Tolman, *Chem. Rev., 7* (1977) 313.