Synthesis of Manganese and Rhenium Half-Sandwich Complexes with Cp-Phosphaferrocene Ligands

Joachim Bitta, Stefan Fassbender, Guido Reiss,§ Walter Frank,§ and Christian Ganter*

Institut für Anorganische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

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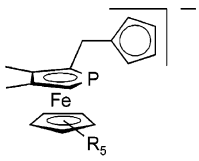
Summary: The phosphaferrocene-substituted Cp anion ***1*** *has been used to prepare the tricarbonyl half-sandwich complexes* ***1***·*M(CO)$_3$ (****2****, M = Mn;* ***3****, M = Re), which release one CO ligand upon irradiation and transform to the respective dicarbonyl complexes* ***4*** *and* ***5*** *with the phosphaferrocene donor group coordinated in an intramolecular chelating manner. Due to the chirality of the phosphaferrocene moiety, subsequent photolytic substitution of a further CO ligand in the manganese complex* ***4*** *by a PPh$_3$ leads to a 11:1 mixture of diastereomers of the monocarbonyl complex* ***6****.*

Introduction

Cyclopentadienyl ligands bearing suitable donor groups are valuable building blocks for the assembly of half-sandwich complexes.[1] If the Cp substituent is a chiral entity, the formation of complexes with defined configuration of the stereogenic metal center via intramolecular chelation becomes possible.[2] In previous papers we have demonstrated the use of the planar chiral phosphaferrocene bearing Cp ligands **1a**,**b**—employed as either the sodium or thallium salts, respectively—for the synthesis of chiral ruthenium half-sandwich complexes, where the phosphaferrocene donor is coordinated in an intramolecularly chelating fashion, which allows a high degree of stereocontrol at the Ru atom.[3] In this contribution we describe the formation of Cp manganese and rhenium half-sandwich complexes employing the chiral ligand **1a** as its thallium salt. All investigations were carried out with the racemic mixture of anion **1**. However, gram amounts of the enantiomerically pure starting material 2-formyl-3,4-dimethylphosphaferrocene are available via resolution,[4] so that enantiopure ligand **1a** can be prepared if desired.

Chart 1



1a, R = H

1b, R = Me

Results and Discussion

While the reaction of Na-**1a** with M(CO)$_5$Br (M = Mn, Re) was unsuccessful and did not lead to an isolable product, the analogous procedure with the thallium salt Tl-**1a** proceeded straightforwardly when the mixture was heated in toluene to 70−85 °C for 40 min until the evolution of CO had ceased. The tricarbonyl half-sandwich complexes **1a**·M(CO)$_3$ (**2**, M = Mn; **3**, M = Re) were isolated from the crude mixture in excellent yields (>95%) as orange-yellow solids. ^{31}P resonances for both complexes around −77 ppm indicated noncoordinated phosphorus atoms of the phosphaferrocene units.

In the next step one CO ligand could be released from the tricarbonyl complexes with concomitant intramolecular coordination of the phosphaferrocene donor. Thus, irradiation of the manganese tricarbonyl **2** in hot THF gave the anticipated dicarbonyl chelate complex **4**, which was obtained in 68% yield after chromatographic workup as red crystals. In the ^{31}P NMR spectrum the coordination of the P atom leads to the usual characteristic changes: a significant downfield shift of ca. 150 ppm and a reduction of the $^2J_{HP}$ coupling constant for the α phospholyl H from 36 Hz in **2** to 32 Hz in chelate complex **4** are observed. The analogous Re chelate complex **5** could be synthesized starting from tricarbonyl **3** according to the same procedure and featured comparable analytic data. However, the downfield shift of the ^{31}P resonance due to coordination amounts to only 70 ppm in the case of Re complex **5**. Crystals of complexes **4** and **5** suitable for X-ray diffraction analysis were obtained by slowly cooling hexane/ether solutions. The two compounds are isostructural and crystallize in the monoclinic spacegroup *I*2/*a* with $Z = 8$. An ORTEP representation of the molecular structure of the Mn complex **4** is shown in Figure 1; the

* Corresponding author. E-mail: christian.ganter@uni-duesseldorf.de.

§ X-ray structure determinations.

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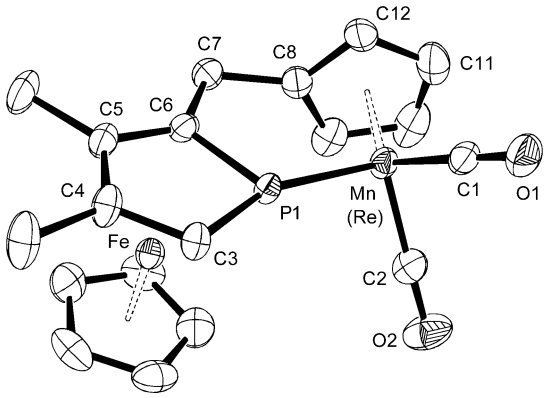
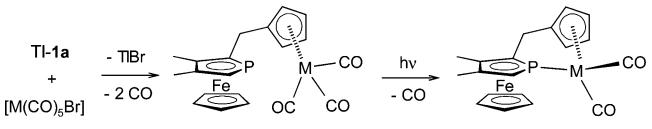


Figure 1. ORTEP view of the molecular structure of **4**. H atoms have been omitted for clarity.

Scheme 1



2 (M = Mn)
3 (M = Re)
4 (M = Mn)
5 (M = Re)

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4 and 5

	4 (M = Mn)	**5** (M = Re)
M−P1	2.2007(9)	2.2974(12)
M−C1	1.788(4)	1.906(6)
M−C2	1.769(4)	1.895(6)
C1−O1	1.151(4)	1.164(7)
C2−O2	1.160(4)	1.155(7)
P1−C3	1.756(3)	1.751(5)
P1−C6	1.751(3)	1.758(5)
P1−M−C1	99.13(11)	98.51(16)
P1−M−C2	97.41(11)	97.00(17)
C1−M−C2	90.66(17)	89.1(2)
C3−P1−M	157.54(11)	157.46(18)
C6−P1−M	111.66(12)	110.94(18)
C3−P1−C6	90.76(16)	91.5(2)

gross structural features of the Re compound **5** are identical to those of the Mn complex. Relevant geometrical data of both structures are compiled in Table 1. The structure features a virtually perpendicular arrangement of the phospholyl ligand with respect to the Cp ring at the Mn atom. The phospholyl ring plane intersects the OC−Mn−CO angle in a symmetrical fashion. The Mn atom lies in the phospholyl ring plane but is tilted to a considerable extent from the ideal position, pointing radially away from the P atom. The angles of 111.7° (C6−P−Mn) and 157.5° (C3−P−Mn) suggest a significant degree of steric strain in the structure, which is due to the incorporation of the phosphaferrocene unit into the chelate ligand architecture. Comparable distortions for phosphaferrocene containing chelate ligands have been found before.[5] As is usually observed for coordinated phosphaferrocenes, the metal−P bond (Mn−P: 220.1 pm) is slightly shorter than in the case of trialkyl or triaryl phosphine ligands and somewhat longer than in the case of phosphite complexes with $P(OR)_3$ ligands (compare for example with Mn−P (pm) in $C_5H_4MeMn(CO)_2PPh_3$ (223.2),[6] $C_5Me_5Mn(CO)_2PMe_3$ (222.0),[7] $\{Fe(C_5H_4)_2PPh\}Mn(C_5Me_5)(CO)_2$(221.1),[8] $[C_7H_6C_5H_4Mn(CO)_2(P\{OMe\}_3)]BF_4$(217.9),[9] $C_5H_4MeMn(CO)_2\{P(OR)_3\}$ (213.8 and 213.4)[10]). The Mn−C bonds to the carbonyl ligands (176.9 and 178.8 pm) lie in the typical range for half-sandwich manganese carbonyl complexes[6−10] with an almost linear M−CO arrangement (176.2° and 177.7°). The angle C1−Mn−C2 is perpendicular (90.7°). Due to the greater radius of the Re atom, all bonds in complex **5** involving Re are longer than the respective ones with Mn in complex **4**. The Re−CO distances (190.6 and 189.5 pm) and the Re−P bond (229.7 pm) are in good agreement with literature data for related compounds (compare for example $C_5Me_4CH_2C_4H_3SRe(CO)_2PMe_3$: Re−P (234.2 pm), Re−CO (188.2 and 189.1 pm);[11] $C_5H_4(CH_2)_2NMeCH_2PPh_2Re(CO)_2$: Re−P (233.1 pm), Re−CO (188.6 and 187.4 pm);[12] $[(C_5Me_4CH_2PMe_3)Re(CO)_2PMe_3^+]I^-$: Re−P (234.7 pm), Re−CO (188.3 and 188.5 pm)[13]).

Replacement of one of the diastereotopic carbonyl ligands in complex **3** or **5** by another donor leads to a half-sandwich complex with a stereogenic metal atom. We were interested in whether the presence of the chiral phosphaferrocene moiety would lead to a certain degree of selectivity in such a substitution reaction. Thus, the replacement of a CO by triphenylphosphine was investigated. Photolysis of the Mn complex **4** in the presence of 1 equiv of PPh_3 led to the formation of the two diastereomeric complexes **6a** and **6b** in a ratio of 11:1 (83% de) as determined by ^{31}P NMR spectroscopy of the crude reaction mixture. The diastereomeric ratio did not change when the mixture was heated to reflux in xylene overnight, and therefore a decision whether the isomer ratio is under thermodynamic or kinetic control can currently not be made. Red crystals of the major diastereomer **6a** were obtained from this solution after cooling. Recrystallization from xylene gave crystals suitable for X-ray diffraction. Complex **6a** crystallizes in the monoclinic space group $P2_1/n$ as a solvate with one molecule of *p*-xylene located on an inversion center. ORTEP drawings of the molecular structure are depicted in Figures 2 and 3 together with relevant geometrical data. Isomer **6a** is obviously the thermodynamically more stable isomer, because the PPh_3 ligand has taken up the position of the carbonyl group where the interference with the phosphaferrocene moiety is least (*trans* to the CpFe moiety, see Figure 3). Compared with the dicarbonyl complex **4**, the Mn−P1 bond to the phosphaferrocene donor in complex **6a** is reduced by 3.2 pm to 216.9 pm, reflecting the higher degree of π-backbonding from the metal due to the increased electron density at Mn in the PPh_3 complex **6a**. The Mn−C distance to the CO ligand is not significantly affected

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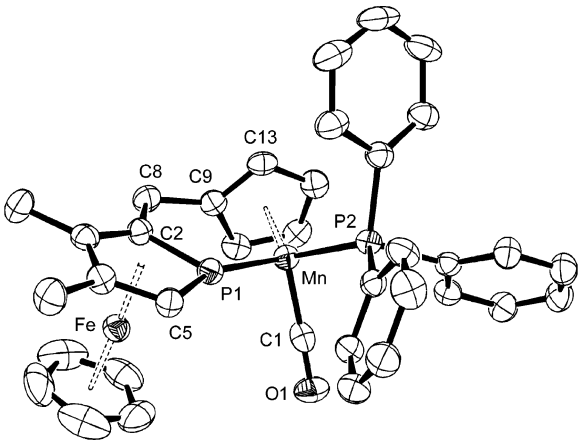


Figure 2. ORTEP view of the molecular structure of **6a**. The solvating *p*-xylene and H atoms have been omitted for clarity. Selected bond lengths (Å): Mn−P1 2.1688(12), Mn−P2 2.2146(11), Mn−C1 1.758(5), C1−O1 1.171(4), P1−C5 1.740(4), P1−C2 1.755(3). Selected angles (deg): P1−Mn−P2 98.76(5), P1−Mn−C1 95.41(13), P2−Mn−C1 93.47(12), Mn−P1−C2 112.23(15), Mn−P1−C5 157.17(13), C2−P1−C5 90.58(19).

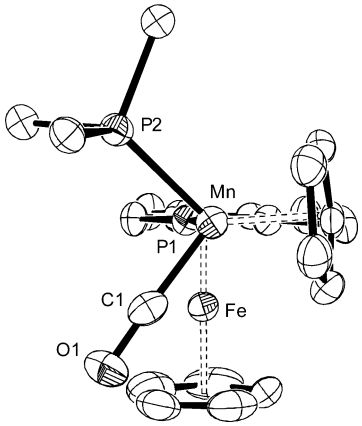
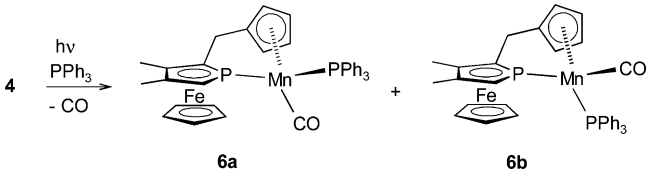


Figure 3. View of the molecular structure of **6a** down the P1−Mn axis. For the phenyl rings only the *ipso*-C atoms are shown for clarity.

by the substitution. The two Mn−P distances differ considerably, by about 4.5 pm, with the bond to the phosphaferrocene P atom being shorter (Mn−P1: 216.9 pm; Mn−P2: 221.5 pm), while the Mn−P distance to the PPh_3 ligand is in the range usually observed for other Mn−PPh_3 complexes. Literature reports on Cp-Mn(CO) complexes with two P ligands are rare; illustrative examples are $\{Cr(C_6H_5PMe_2)_2\}MnCp(CO)$[14] and $CpMn(CO)(Cl_2PCH_2CH_2PCl_2)$.[15] In the former compound the Mn−P distances are 219.3 and 218.4 pm, while in the latter complex the stronger acceptor properties of the bis(dichlorophosphine) ligand lead to shorter Mn−P bonds of 210.6 and 211.3 pm, respectively. No conditions could be found to transform the Re complex **5** into a similar substitution product with triphenylphoshine.

We are currently exploring the synthesis of phosphaferrocene-containing cationic manganese and rhenium half-sandwich complexes with stereogenic metal atoms which may serve as chiral Lewis acid catalysts after

Scheme 2



6a **6b**

removal of a loosely bound ligand from the metal. However, all attempts to obtain such cationic species where a CO ligand is replaced by a NO^+ group starting from complexes **2**−**5** described in this paper failed. A successful synthetic alternative is therefore currently under development and will be published elsewhere.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dry nitrogen by means of conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 220 °C for 12 h, cooled to room temperature under high vacuum, deactivated with 5% water, and stored under nitrogen. NMR spectra were recorded on a Bruker Avance DRX 500 (^{1}H, 500 MHz; $^{31}P\{^1H\}$, 202 MHz; $^{13}C\{^1H\}$, 126 MHz) and a Bruker Avance DRX 200 spectrometer (^{1}H, 200 MHz; $^{31}P\{^1H\}$, 81 MHz). ^{1}H spectra are referenced to the residual solvent signal and ^{31}P spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Varian MAT 311A spectrometer (EI, 70 eV electron energy). Irradiations were carried out using a Heraeus TQ 150 medium-pressure Hg lamp. Tl-**1a**[3b] and $M(CO)_5Br$[16] were synthesized according to literature procedures.

Synthesis of Manganese Tricarbonyl Complex 2. To Tl-**1a** (0.55 g, 1.07 mmol) and $Mn(CO)_5Br$ (0.29 g, 1.07 mmol) was added toluene (25 mL). After stirring at 70 °C for 40 min the suspension was evaporated to dryness. Subsequent purification of the resulting solid by chromatography on alumina with hexane/diethyl ether (2:1) afforded the pure product as an orange powder (0.47 g, 98%). ^{1}H NMR (200 MHz, $CDCl_3$): 2.22 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 3.00−3.19 (m, 2 H, CH_2), 3.72 (d, ^2J(H,P) = 36.1 Hz, 1 H, phospholyl-α-H), 4.12 (s, 5 H, Cp), 4.56−4.64 (m, 4 H, C_5H_4). ^{13}C NMR (126 MHz, $CDCl_3$): 14.1 (s, CH_3), 17.2 (s, CH_3), 29.7 (d, ^2J(C,P) = 20.6 Hz, CH_2), 72.3 (s, Cp CH), 76.2 (d, ^1J(C,P) = 58.5 Hz, phospholyl-α-CH), 81.6 (s, C_5H_4 CH), 81.9 (s, C_5H_4 CH), 82.7 (s, C_5H_4 CH), 83.3 (s, C_5H_4 CH), 92.9 (d, ^2J(C,P) = 3.9 Hz, phospholyl-β-C(q)), 96.2 (d, ^2J(C,P) = 6.4 Hz, phospholyl-β-C(q)), 98.2 (d, ^1J(C,P) = 58.1 Hz, phospholyl-α-C(q)), 106.1 (s, C_5H_4 C(q)), 225.3 (s, CO). ^{31}P NMR (81 MHz, $CDCl_3$): −77.4 (s). IR: 1931, 2018. MS: 448 (M^+), 364 (M^+ − 3 CO), 310, 245. Anal. Calcd for $C_{20}H_{18}O_3PFeMn$ (448.1): C 53.61, H 4.05. Found: C 53.37, H 4.18.

Synthesis of Manganese Dicarbonyl Complex 4. A solution of **2** (0.52 g, 1.16 mmol) in THF (450 mL) was irradiated for about 25 min at 50 °C. The solvent was removed under vacuum, and the residue was purified by chromatography on alumina (hexane/diethyl ether, 10:1). The product was obtained as a light orange powder (0.33 g, 68%). Recrystallization from diethyl ether/hexane gave red crystals. ^{1}H NMR (200 MHz, $CDCl_3$): 2.09 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.39−2.70 (m, 2 H, CH_2), 3.50 (d, ^2J(H,P) = 32.1 Hz, 1 H, phospholyl-α-H), 4.19 (s, 5 H, Cp) 4.38−4.43 (m, 1 H, C_5H_4), 4.44−4.89 (m, 1 H, C_5H_4), 4.55−4.60 (m, 1 H, C_5H_4), 4.77−4.83 (m, 1 H, C_5H_4). ^{13}C NMR (126 MHz, $CDCl_3$): 14.2 (d, ^3J(C,P) = 3.6 Hz, CH_3), 16.6 (d, ^3J(C,P) = 6.1 Hz, CH_3), 24.6 (d, ^2J(C,P) = 21.8 Hz, CH_2), 65.8 (d, ^1J(C,P) = 4,9 Hz, phospholyl-α-CH), 74.4 (s, Cp CH), 78.3 (s, C_5H_4 CH), 78.5 (s, C_5H_4 CH), 78.5 (s, C_5H_4 CH), 81.4 (s, C_5H_4 CH), 88.5 (d, ^2J(C,P) = 6.1 Hz, phospholyl-α-C(q)), 89.2 (s, C_5H_4 C(q)), 111.1 (d, ^2J(C,P) = 8.5 Hz, phospholyl-β-C(q)), 123.6 (d, ^2J(C,P) = 7.3 Hz, phospholyl-β-C(q)), 232.1 (s, CO), 233.1 (s, CO). ^{31}P NMR (81 MHz, $CDCl_3$): 71.7 (s). IR: 1940, 1876. MS: 420 (M^+), 364

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Table 2. Crystallographic Data for 4, 5, and 6a

	4	**5**	**6a**·$^1/_2$(*p*-xylene)
formula	$C_{19}H_{18}FeMnO_2P$	$C_{19}H_{18}FeReO_2P$	$C_{40}H_{38}FeMnOP_2$
fw	420.09	551.36	707.43
cryst syst	monoclinic	monoclinic	monoclinic
space group	*I*2/*a*	*I*2/*a*	$P2_1/n$
a, Å	18.6315(12)	18.8039(10)	9.3554(11)
b, Å	9.6162(5)	9.5428(5)	14.381(3)
c, Å	19.3704(12)	19.6102(9)	25.319(4)
β, deg	99.633(6)	99.243(5)	91.73(3)
V, Å^3	3421.6(4)	3473.2(3)	3404.9(10)
d_{calcd}, g·cm^{-3}	1.631	2.109	1.380
Z	8	8	4
F(000)	1712	2112	1468
μ, cm^{-1}	16.87	78.99	9.22
cryst dimens, mm	0.18 × 0.15 × 0.07	0.11 × 0.06 × 0.05	0.48 × 0.43 × 0.36
T, K	293	293	293
scan mode	*ω*	*ω*	*φ*
scan range, deg	2.2 < *θ* < 27.5	6.8 < *θ* < 27.5	2.1 < *θ* < 26.0
no. of reflns measd	22 262	22 487	23 954
total no. of data	3896	3974	6427
no. of obsd data	3051 ($I > 2\sigma(I)$)	3411 ($I > 2\sigma(I)$)	2740 ($I > 2\sigma(I)$)
no. of variables	221	222	409
R_1 [$I > 2\sigma(I)$],	0.0472	0.0340	0.0412
wR_2 [$w^{-1} = \sigma^2(F_o)$],	0.0888	0.0774	0.0579
GOF	1.068	1.071	0.713
max. resid density, e Å^{-3}	0.394	1.914	0.438

($M^+ - 2$ CO). Anal. Calcd for $C_{19}H_{18}O_2PFeMn$ (420.1): C 54.32, H 4.32. Found: C 54.09, H 4.71.

Synthesis of Rhenium Tricarbonyl Complex 3. To Tl-**1a** (0.71 g, 1.37 mmol) and $Re(CO)_5Br$ (0.56 g, 1.37 mmol) was added toluene (30 mL). After stirring at 85 °C for 45 min the suspension was evaporated to dryness. Subsequent purification of the resulting solid by chromatography on alumina with hexane/diethyl ether (2:1) afforded the pure product as an orange powder (0.76 g, 96%). ^{1}H NMR (200 MHz, $CDCl_3$): 2.22 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 3.20−3.29 (m, 2 H, CH_2), 3.78 (d, ^2J(H,P) = 36.1 Hz, 1 H, phospholyl-α-H), 4.16 (s, 5 H, Cp), 5.20−5.32 (m, 4 H, C_5H_4). ^{13}C NMR (126 MHz, $CDCl_3$): 14.1 (s, CH_3), 17.2 (s, CH_3), 29.6 (d, ^2J(C,P) = 21.8 Hz, CH_2), 72.4 (s, Cp CH), 76.2 (d, ^1J(C,P) = 58.2 Hz, phospholyl-α-CH), 83.3 (s, C_5H_4 CH), 83.7 (d, J = 2.4 Hz, C_5H_4 CH), 83.8 (s, C_5H_4 CH), 84.3 (s, C_5H_4 CH), 92.8 (d, ^2J(C,P) = 4.9 Hz, phospholyl-*β*-C(q)), 96.3 (d, ^2J(C,P) = 7.3 Hz, phospholyl-*β*-C(q)), 98.3 (d, ^1J(C,P) = 59.5 Hz, phospholyl-α-C(q)), 110.0 (s, C_5H_4 C(q)), 194.7 (s, CO). ^{31}P NMR (81 MHz, $CDCl_3$): −76.9 (s). IR: 1923, 2021. MS: 580 (M^+), 552 ($M^+ - CO$), 496 ($M^+ - 3$ CO). Anal. Calcd for $C_{20}H_{18}O_3PFeRe$ (579.4): C 41.46, H 3.13. Found: C 41.63, H 3.26.

Synthesis of Rhenium Dicarbonyl Complex 5. A solution of **3** (0.83 g, 1.43 mmol) in THF (450 mL) was irradiated in a quartz apparatus for about 1 h at 50 °C. The solvent was removed under vacuum, and the residue was purified by chromatography on alumina (hexane/diethyl ether, 8:1). The product was obtained as a light orange powder (0.35 g, 44%). Recrystallization from ether/hexane gave red crystals. ^{1}H NMR (200 MHz, $CDCl_3$): 2.11 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.37−2.74 (m, 2 H, CH_2), 3.46 (d, ^2J(H,P) = 32.1 Hz, 1 H, phospholyl-α-H), 4.16 (s, 5 H, Cp) 4.90−4.95 (m, 1 H, C_5H_4), 5.22−5.28 (m, 2 H, C_5H_4), 5.32−5.39 (m, 1 H, C_5H_4). ^{13}C NMR (126 MHz, $CDCl_3$): 1.5(d, ^3J(C,P) = 7.7 Hz, CH_3), 16.5 (d, ^3J(C,P) = 6.1 Hz, CH_3), 24.7 (d, ^2J(C,P) = 27.0 Hz, CH_2), 60.1 (d, ^1J(C,P) = 9.6 Hz, phospholyl-α-CH), 74.6 (s, Cp CH), 78.34 (s, C_5H_4 CH), 78.8 (d, J = 5.8 Hz, C_5H_4 CH), 79.1 (d, J = 8.5 Hz, C_5H_4 CH), 81.3 (s, C_5H_4 CH), 87.3 (d, ^2J(C,P) = 4.8 Hz, phospholyl-α-C(q)), 89.9 (d, ^3J(C,P) = 7.3 Hz, C_5H_4 C(q)), 115.5 (d, ^2J(C,P) = 19.4 Hz, phospholyl-*β*-C(q)), 126.8 (d, ^2J(C,P) = 8.5 Hz, phospholyl-*β*-C(q)), 201.6 (d, ^2J(C,P) = 6.1 Hz, CO), 203.2 (d, ^2J(C,P) = 8.5 Hz, CO). ^{31}P NMR (81 MHz, $CDCl_3$): −5.64 (s). IR: 1932, 1866. MS: 552 (M^+), 496 ($M^+ - 2$ CO). Anal. Calcd for $C_{19}H_{18}O_2PFeRe$ (551.4): C 41.39, H 3.29. Found: C 41.25, H 3.49.

Synthesis of Manganese Complex 6. A solution of **4** (51.8 mg, 0.123 mmol) and PPh_3 (32.3 mg, 0.123 mmol) in *p*-xylene (5 mL) was irridiated for about 1 h in a quartz tube. A ^{31}P NMR spectrum of the reaction mixture indicated a ratio of diastereomers **6a** and **6b** of 11:1 at 65% conversion. After a few days one diastereomer formed dark red crystals that were suitable for X-ray structure determination after recrystallization from xylene. ^{31}P NMR of the reaction mixture after irradiation (202 MHz, $CDCl_3$): major isomer: 84.9 (d, ^2J(P,P) = 38.4 Hz), 101.2 (d, ^2J(P,P) = 38.4 Hz); minor isomer: 86.5 (d, ^2J(P,P) = 38.7 Hz), 99.8 (d, ^2J(P,P) = 38.7 Hz). ^{1}H NMR, major diastereomer (500 MHz, $CDCl_3$): 2.01 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.43 (d, ^2J(H,P) = 30.0 Hz, 1 H, phospholyl-α-H), 2.48−2.53 (m, 2 H, CH_2), 3.19 (s, 1 H, C_5H_4), 3.88 (d, 1 H, J = 6.3 Hz, C_5H_4 CH), 4.19 (s, 5 H, Cp), 4.26 (s, 1 H, C_5H_4), 4.70 (s, 1 H, C_5H_4), 7.27−7.45 (m, 15 H, PPh_3).

X-ray Structure Determinations. Crystals of compounds **4**, **5**, and **6a**·$^1/_2$(*p*-xylene) suitable for X-ray study were investigated with a Stoe CCD diffractometer (**4**, **5**) and a Stoe imaging plate diffraction system (**6a**·$^1/_2$(*p*-xylene)), respectively, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares refinements on the positions of 6380, 6753, and 1195 reflections in the range 6.8° < *θ* < 21.6°, 6.8° < *θ* < 21.5°, and 2.1° < *θ* < 26.0°, respectively. In the case of the isotypic compounds **4** and **5** systematic extinctions were consitent with space groups *Ia* and *I*2/*a*, but the latter proved to be the correct one in the course of structure refinements. Space group $P2_1/n$ was uniquely determined in the case of **6a**·$^1/_2$(*p*-xylene). *Lp* corrections were applied to all the intensity data. In the case of **5** an empirical extinction parameter was refined; in the case of **6a**·$^1/_2$(*p*-xylene) semiempirical absorption corrections had to be applied ($T_{min.}$ = 0.614; $T_{max.}$ = 0.708). The structures were solved by direct methods,[17] and the positions of all but the hydrogen atoms of the methyl groups of the *p*-xylene molecule of **6a**·$^1/_2$(*p*-xylene) were found via ΔF syntheses. Refinements[18] by full-matrix least-squares calculations on F^2 converged to the indicators given in Table 2. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Idealized bond lengths and angles were used for the CH_3, CH_2, and CH groups; the riding model was applied for their H atoms. In addition, the H atoms of the CH_3 groups were allowed to rotate around the neighboring C−C bonds. For the CH_3 groups of **4** and **5** common U_{iso}(H) values were refined. The isotropic displacement parameters of all the other H atoms were kept equal to 150, 130, and 120% of the equivalent isotropic displacement parameters of the parent primary, secondary, and "aromatic" carbon atoms, respectively. A summary of further crystallographic data, data collection parameters, and refinement parameters is collected in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-282830 (**4**), -282831 (**5**), and -282832 (**6a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: int. +1223/336-033; e-mail: teched@chemcrys.cam.ac.uk) or via the Internet at http://www.ccdc.cam.ac.uk.

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Supporting Information Available: X-ray structural information for compounds **4**, **5**, and **6a**. This material is available free of charge via the Internet at http://www.acs.org.

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