Synthesis and Characterization of Manganese and Rhenium Metallacycles

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Reactions of manganese or rhenium formyl complexes bearing phosphine or phosphite ligands with protonic acids have been utilized in developing synthetic routes to new five- and six-membered metallacyclic compounds, $Mn(CO)_4[P(Ph)_2(o\text{-}C_6H_4CH_2)]$ and $M(CO)_3(L)[P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ (M = Mn, L = CO or $P(OPh)_3$; M = Re, L = $P(OPh)_3$). The synthetic route makes use of the ability of formyl complexes to transfer hydride in the presence of a protonic acid without transferring it to the acid. Two of the manganese compounds have been characterized by X-ray crystallography: (i) crystal data for $Mn(CO)_4[P(Ph)_2(o\text{-}C_6H_4CH_2)]$, $a = 13.519$ (3) Å, $b = 8.295$ (2) Å, $c = 18.199$ (3) Å, $\beta = 90.82$ (1)°, $Z = 4$, $d_c = 1.44$ g cm^{-3}, space group $P2_1/c$, and $R = 0.029$; (ii) crystal data for $Mn(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$, $a = 15.977$ (8) Å, $b = 26.554$ (10) Å, $c = 8.523$ (6) Å, $\beta = 87.12$ (5)°, $Z = 4$, $d_c = 1.42$ g cm^{-3}, space group $P2_1/n$, and $R = 0.039$. The IR and ^1H and ^{13}C NMR spectral properties of all four metallacycles are reported.

Introduction

There have been several types of strategies employed in synthesizing five-membered metallacyclic compounds having a metal–carbon σ bond and a phosphorous atom associated with the ring system. For example, cyclometalated products were reported to result from heating $CH_3Mn(CO)_5$ or $C_6H_5CH_2M(CO)_5$ (M = Mn, Re) with an aryl phosphine substituted at one ortho position by an alkyl group as illustrated in eq 1.[1-3] Similar five-membered products have resulted from reactions involving rhodium, ruthenium, iron, gold[4a-d] and also platinum[5,6] and palladium[4e,5,6] complexes; these procedures could not be extended to six-membered compounds by use of phosphites instead of phosphines. Gladysz[3] also generated a five-membered manganese metallacycle by treating a phosphine-substituted aldehyde with $HMn(CO)_5$. Other five-membered complexes have been obtained through Friedel–Crafts-like electrophilic substitution reactions; in these cases the electrophilic carbon atom was generated by removal of halide ion from a σ-bonded carbon ligand[7,8] or by loss of N_2 from a diazo compound.[8f]

$$CH_3Mn(CO)_5 + P(o\text{-}C_6H_4CH_3)_3 \xrightarrow[\Delta]{-CO} Mn(CO)_4[P(o\text{-}C_6H_4CH_3)_2(o\text{-}C_6H_4CH_2)] + CH_4 \quad (1)$$

Herein we report the synthesis and characterization of new five- and six-membered metallacyclic complexes by proton-promoted cyclometalation reactions involving manganese and rhenium formyl complexes.[9] The new metallacyclic compounds and their formyl precursors are shown in Chart I; the preparations of the formyl complexes have been described previously.[10]

Results and Discussion

Synthesis of Metallacycles. The synthesis of each metallacyclic compound results from the rapid reaction of a neutral manganese or rhenium formyl complex with a strong protonic acid. On the basis of our own work[9,11] as well as that of others,[12] the reaction path is believed to be as shown in eq 2 for compound **5**. As the equation in-

$$\underset{\mathbf{1}}{OHC{-}Mn(CO)_4(PPh_3)} \xrightarrow{H^+} \underset{\mathbf{a}}{HOHC{=}Mn(CO)_4(PPh_3)^+} \xrightarrow[-Mn(CO)_5(PPh_3)^+]{\mathbf{1}} \underset{\mathbf{b}}{HOH_2C{-}Mn(CO)_4(PPh_3)} \xrightarrow{H^+,\ -H_2O} \underset{\mathbf{c}}{H_2C{=}Mn(CO)_4(PPh_3)^+} \xrightarrow{-H^+} \underset{\mathbf{5}}{Mn(CO)_4[P(Ph)_2(o\text{-}C_6H_4CH_2)]} \quad (2)$$

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Chart I. Metallacycles and Formyl Precursors

formyl complex	metallacycle
cis-$Mn(CO)_4(PPh_3)CHO$ 1	$Mn(CO)_4[P(Ph_2)(o\text{-}C_6H_4CH_2)]$ 5
cis-$Mn(CO)_4[P(OPh)_3]CHO$ 2	$Mn(CO)_4[P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ 6
mer,trans-$Mn(CO)_3[P(OPh)_3]_2CHO$ 3	$Mn(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ 7
mer,trans-$Re(CO)_3[P(OPh)_3]_2CHO$ 4	$Re(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ 8

dicates, 1 mol of the formyl complex is sacrificed as a result of hydride donation to the hydroxymethylidene cation a. However, the carbonyl cation generated by this hydride transfer [e.g., $Mn(CO)_5(PPh_3)^+$ in eq 2] is the precursor to the formyl complex in each case and it can be recycled to improve the overall yield. On the basis of the reaction stoichiometry indicated, the yields of metallacycles are 60–92%. Hydride transfer from the formyl complex to the protonic acid does not occur as a competing reaction in any case.

Support for the initial step in eq 2 is found from studying the behavior of the bisphosphine analogue of 1, *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$ (9), with strong acids such as HBF_4 and *p*-toluenesulfonic acid. In these cases, the hydroxymethylidene cations (analogues of a in eq 2) are isolable and have been characterized.[9] Further reaction of either of these with formyl complex 9 does not occur. Although 9 would be expected to be a better hydride donor than its monophosphine analogue, 1, the limiting factor in further conversion of 9 appears to be the reduced electrophilic behavior of $Mn(CO)_3(PPh_3)_2(CHOH)^+$. The electronic balance between these two requirements is apparently better with the bisphosphite formyl complex, 3, whose reaction cannot be stopped at the hydroxymethylidene stage and proceeds directly to metallacycle 7.

Support for the formation of hydroxymethyl intermediate b from 1 and a is available, indirectly, from the observed reductions of methoxymethylidene cations to methoxymethyl complexes by formyl complexes.[9,12b] Also, the formation of $M-CH_2OH$ species by hydride reduction of formyl complexes is well-known.[12] The possible formation of methylidene cations such as c from reactions between formyl complexes and electrophiles was first detailed by Gladysz.[12] In the present work, the formation of compound 10, *cis*-$Mn(CO)_4(PPh_3)CH_2OC(O)CF_3$, from 1 and CF_3COOH can be taken as support for the intermediacy of c (metallacycle 5 is stable to CF_3COOH). In other cases, the electrophile-promoted disproportionations of formyl complexes have led to methyl complexes (together with 2 equiv of the metal carbonyl cation); the final step in these reactions appears to be hydride transfer (from the formyl) to an intermediate methylidene cation.[12]

Although trifluoroacetic acid can be used for the synthesis of all four metallacycles, the yield of 5 is diminished by the partitioning of intermediate c between 10 and the metallacycle. Compounds 5 and 10 are formed in nearly equal amounts when CF_3COOH is used, whereas HBF_4 provides a 74% yield of 5.

Characterization of the Metallacycles. Acceptable elemental analyses were obtained for 5–8 (see Experimental Section). Crystallographic data were obtained for 5 and 7; the other two were characterized by use of analytical and spectral data.

Table I. Summary of Crystallographic Data for $Mn(CO)_4[P(Ph)_2(o\text{-}C_6H_4CH_2)]$ (5) and $Mn(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ (7)

	5	7
formula	$C_{23}H_{16}O_4PMn$	$C_{40}H_{31}O_9P_2Mn$
formula wt	442.29	772.57
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	13.519 (3)	15.977 (8)
b, Å	8.295 (2)	26.554 (10)
c, Å	18.199 (3)	8.523 (6)
β, deg	90.82 (1)	87.12 (5)
vol, $Å^3$	2040.5	3611.2
Z	4	4
D_c, g/cm^3	1.44	1.42
cryst dimens, mm	0.21 × 0.45 × 0.51	0.21 × 0.31 × 0.49
cryst descn	pale yellow plate	pale yellow plate, cut
μ(Mo Kα), cm^{-1}	7.2	4.9
radtn	Mo Kα (λ 0.710 73)	Mo Kα (λ 0.710 73)
diffractometer	CAD4	CAD4
monochromator	graphite	graphite
temp, °C	23 (1)	23 (1)
scan range	$0.70 + 0.34 \tan \theta$	$1.5(0.70 + 0.34 \tan \theta)$
scan speed, deg min^{-1}	1–3	1–3
max θ, deg	25	22.5
intensity decay, %	1.7	4.2, corrected
no. of unique reflctns collected	3695	4715
no. of rflctns obsd ($I > 3\sigma(I)$)	2842	3547
computing	SDP/VAX	SDP/VAX
weighting formula	$4F_o^2/[\sigma(F_o^2)]^2$	$4F_o^2/[\sigma(F_o^2)]^2$
p	0.04	0.04
no. of variables	263	470
no. of observns	2842	3547
max Δ/σ	0.02	0.02
GOF	1.60	1.85
ext coeff	$3 (1) \times 10^{-7}$	$8 (2) \times 10^{-8}$
resid ed, e $Å^{-3}$	0.27 (4)	0.40 (5)
agreement factors		
R	0.029	0.039
R_w	0.033	0.049

A. X-ray Crystal Structures of 5 and 7. Single-crystal X-ray data were obtained for compound 5 under the conditions summarized in Table I; the unit cell was found to be monoclinic. Refinement, described in the Experimental Section, included location of the hydrogen atoms from a difference Fourier map. An ORTEP representation of 5 is shown in Figure 1; bond distances and bond angles are compiled in Table II. Positional parameters are given in Table III. Note, in particular, that the P–Mn–C(5) angle (77.60°) is greatly compressed from theory (90°) and that the P–Mn–C(4) angle (164.88°) is also compressed; both demonstrate distortion from octahedral geometry caused by the chelating group. Similarly, the X-ray data obtained for 7 are also summarized in Table I; again, the unit cell was monoclinic. Refinement is described in the Experimental Section and, as above, in-

Table II. Selected Bond Distances and Bond Angles for Compound 5[a]

Distances, Å

atom 1	atom 2	dist	atom 1	atom 2	dist
Mn	P	2.3023 (7)	O2	C2	1.144 (3)
Mn	C1	1.854 (2)	O3	C3	1.143 (3)
Mn	C2	1.830 (2)	O4	C4	1.133 (3)
Mn	C3	1.817 (3)	C5	C12	1.498 (3)
Mn	C4	1.830 (2)	C11	C12	1.396 (3)
Mn	C5	2.188 (2)	C11	C16	1.396 (3)
P	C11	1.810 (2)	C12	C13	1.396 (3)
P	C21	1.834 (2)	C13	C14	1.376 (4)
P	C31	1.824 (2)	C14	C15	1.387 (4)
O1	C1	1.128 (3)	C15	C16	1.388 (3)

Angles, deg

atom 1	atom 2	atom 3	angle
P	Mn	C1	90.05 (8)
P	Mn	C2	91.26 (8)
P	Mn	C3	97.98 (8)
P	Mn	C4	164.88 (8)
P	Mn	C5	77.60 (7)
C1	Mn	C2	173.3 (1)
C1	Mn	C3	93.0 (1)
C1	Mn	C4	88.2 (2)
C1	Mn	C5	90.94 (9)
C2	Mn	C3	93.4 (2)
C2	Mn	C4	88.9 (2)
C2	Mn	C5	82.93 (9)
C3	Mn	C4	97.1 (1)
C3	Mn	C5	174.1 (2)
C4	Mn	C5	87.4 (1)
Mn	P	C11	102.86 (7)
Mn	P	C21	122.89 (8)
Mn	P	C31	114.27 (7)
Mn	C1	O1	177.0 (2)
Mn	C2	O2	177.0 (2)
Mn	C3	O3	178.0 (2)
Mn	C4	O4	177.0 (2)
Mn	C5	C12	112.4 (1)
P	C11	C12	112.1 (2)
P	C11	C16	126.2 (2)
C12	C11	C16	121.8 (2)
C5	C12	C11	118.4 (2)
C5	C12	C13	123.8 (2)
C11	C12	C13	117.8 (2)
C12	C13	C14	120.7 (2)
C13	C14	C15	121.2 (2)
C14	C15	C16	119.4 (2)
C11	C16	C15	119.2 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

cluded the location of the hydrogen atoms from a difference Fourier map. An ORTEP representation of 7 is shown in Figure 2; bond distances and bond angles are compiled in Table IV. Positional parameters are given in Table V. The P(1)–Mn–C(4) angle is considerably larger (83.61°) than the corresponding angle in 5 due to the larger metallacyclic ring. The P(1)–Mn–P(2) angle is somewhat compressed (170.19°), while the angles between the orthogonal carbonyl groups are somewhat larger than a typical octahedral structure. The metallacyclic ring is slightly puckered with a line between O(2) and C(4) defining the intersection of two planes; one plane contains O(2), C(21), C(22), and C(4), while the other contains C(4), Mn, P(1), and O(2). Complete tables of anisotropic thermal parameters, hydrogen atom parameters, and structure factors for 5 and 7 are given in the supplementary material together with expanded tables of bond distances and angles (see the paragraph at the end of the paper).

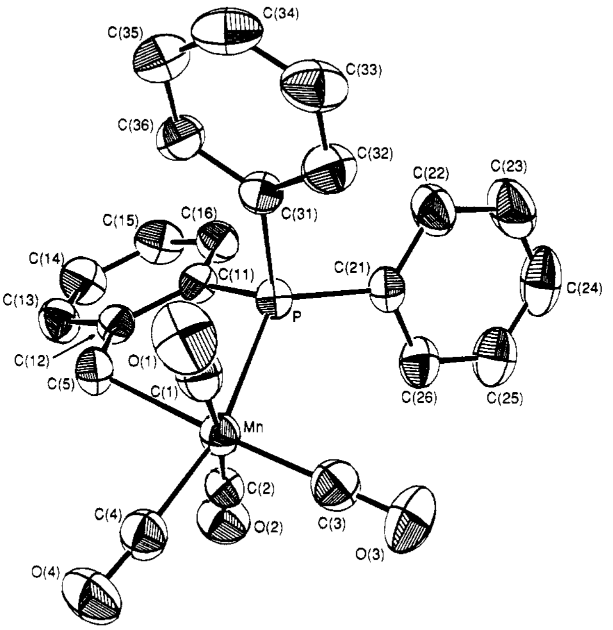

Figure 1. Molecular structure of compound 5, $\overline{\mathrm{Mn(CO)_4[P(Ph)_2(}o\mathrm{\text{-}C_6H_4CH_2}}\mathrm{)]}$. Ellipsoids are drawn at the 50% probability level.

Table III. Positional Parameters and Their Estimated Standard Deviations for Compound 5[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mn	0.20297 (2)	0.12995 (4)	0.06986 (2)	2.844 (6)
P	0.28183 (4)	−0.11578 (7)	0.07605 (3)	2.65 (1)
O1	0.1875 (1)	0.1080 (3)	−0.09338 (9)	5.77 (5)
O2	0.1881 (1)	0.1491 (2)	0.23245 (9)	4.58 (4)
O3	0.3808 (1)	0.3377 (3)	0.0664 (1)	6.56 (5)
O4	0.0513 (1)	0.3869 (2)	0.0598 (1)	5.87 (5)
C1	0.1942 (2)	0.1121 (3)	−0.0316 (1)	3.79 (5)
C2	0.1964 (2)	0.1403 (3)	0.1701 (1)	3.20 (4)
C3	0.3123 (2)	0.2570 (3)	0.0664 (1)	4.12 (5)
C4	0.1112 (2)	0.2918 (3)	0.0640 (1)	3.90 (5)
C5	0.0795 (2)	−0.0378 (3)	0.0825 (1)	3.28 (5)
C11	0.2016 (2)	−0.2328 (3)	0.1343 (1)	2.84 (4)
C12	0.1046 (2)	−0.1752 (3)	0.1329 (1)	2.85 (4)
C13	0.0364 (2)	−0.2497 (3)	0.1787 (1)	3.75 (5)
C14	0.0646 (2)	−0.3755 (3)	0.2236 (1)	4.32 (5)
C15	0.1609 (2)	−0.4334 (3)	0.2240 (1)	4.13 (5)
C16	0.2301 (2)	−0.3623 (3)	0.1787 (1)	3.47 (5)
C21	0.4059 (2)	−0.1416 (3)	0.1164 (1)	3.11 (4)
C22	0.4704 (2)	−0.2584 (3)	0.0929 (2)	4.59 (6)
C23	0.5614 (2)	−0.2775 (4)	0.1291 (2)	5.85 (7)
C24	0.5859 (2)	−0.1843 (4)	0.1886 (2)	5.89 (7)
C25	0.5209 (2)	−0.0693 (4)	0.2132 (2)	5.14 (6)
C26	0.4317 (2)	−0.0463 (3)	0.1762 (1)	4.12 (5)
C31	0.2849 (2)	−0.2244 (3)	−0.0110 (1)	3.05 (4)
C32	0.3549 (2)	−0.1865 (3)	−0.0635 (1)	4.26 (5)
C33	0.3506 (2)	−0.2573 (4)	−0.1323 (1)	5.11 (6)
C34	0.2759 (2)	−0.3638 (3)	−0.1495 (1)	5.22 (7)
C35	0.2060 (2)	−0.4021 (3)	−0.0988 (2)	4.93 (6)
C36	0.2110 (2)	−0.3339 (3)	−0.0287 (1)	3.92 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

B. Spectral Properties. Compounds 5–8 were characterized by IR and by ^{1}H and ^{13}C NMR spectroscopy. IR spectra, in the carbonyl region, for compounds 5 and 6 exhibited four bands (see Experimental Section) with medium, strong, very strong, and strong intensities characteristic of a *cis*-M(CO)$_4$LL′ complex.[13] Compounds 7 and 8 showed three carbonyl bands with weak, strong, and medium intensities expected for a *mer*,*trans*-M(CO)$_3$LL′L″ complex.[14]

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Table IV. Selected Bond Distances and Bond Angles for Compound 7[a]

Distances, Å

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mn	P1	2.203 (1)	P1	O3	1.603 (3)	C4	C22	1.482 (5)
Mn	P2	2.209 (1)	P2	O4	1.604 (2)	C21	C22	1.384 (5)
Mn	C1	1.793 (4)	P2	O5	1.616 (2)	C21	C26	1.373 (5)
Mn	C2	1.817 (4)	P2	O6	1.609 (2)	C22	C23	1.439 (6)
Mn	C3	1.850 (4)	O10	C1	1.152 (5)	C23	C24	1.384 (6)
Mn	C4	2.207 (4)	O20	C2	1.149 (5)	C24	C25	1.369 (7)
P1	O1	1.612 (2)	O30	C3	1.139 (4)	C25	C26	1.384 (6)
P1	O2	1.612 (2)						

Angles, deg

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P1	Mn	P2	170.19 (4)	Mn	P2	O6	122.41 (9)
P1	Mn	C1	91.6 (2)	O4	P2	O5	102.0 (1)
P1	Mn	C2	92.3 (1)	O4	P2	O6	103.7 (1)
P1	Mn	C3	89.5 (2)	O5	P2	O6	97.0 (1)
P1	Mn	C4	83.61 (9)	P1	O1	C11	129.3 (2)
P2	Mn	C1	98.0 (2)	P1	O2	C21	117.6 (3)
P2	Mn	C2	88.8 (1)	P1	O3	C31	123.2 (2)
P2	Mn	C3	88.3 (2)	P2	O4	C41	124.4 (2)
P2	Mn	C4	86.79 (9)	P2	O5	C51	125.7 (3)
C1	Mn	C2	94.6 (2)	P2	O6	C61	126.0 (2)
C1	Mn	C3	93.0 (2)	Mn	C1	O10	176.3 (3)
C1	Mn	C4	175.1 (1)	Mn	C2	O20	176.0 (3)
C2	Mn	C3	172.2 (2)	Mn	C3	O30	179.1 (4)
C2	Mn	C4	84.5 (2)	Mn	C4	C22	110.3 (2)
C3	Mn	C4	88.1 (1)	O2	C21	C22	117.2 (3)
Mn	P1	O1	112.00 (9)	O2	C21	C26	118.1 (3)
Mn	P1	O2	116.99 (9)	C22	C21	C26	124.8 (3)
Mn	P1	O3	123.30 (9)	C4	C22	C21	122.4 (3)
O1	P1	O2	104.3 (1)	C4	C22	C23	122.3 (3)
O1	P1	O3	104.0 (1)	C21	C22	C23	115.2 (3)
O2	P1	O3	93.4 (1)	C22	C23	C24	120.4 (4)
Mn	P2	O4	111.87 (9)	C23	C24	C25	120.9 (4)
Mn	P2	O5	117.0 (1)	C24	C25	C26	120.8 (4)
				C21	C26	C25	118.1 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

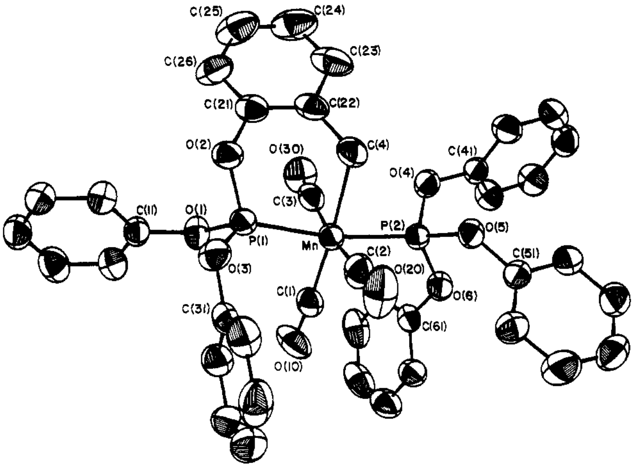

Figure 2. Molecular structure of 7, $Mn(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$. Ellipsoids are drawn at the 50% probability level.

The ^1H and proton-decoupled ^{13}C NMR spectral data for the metallacycles are summarized in Table VI. The methylene protons of 5–8 appear in the region δ 2.0–2.6; 5 and 6 show doublets and 7 and 8 show pairs of doublets as a result of coupling to phosphorus. The chemical shifts of the methylene carbons vary from δ 18.10 to −8.55, with manganese complex 5 showing this carbon at lowest field and rhenium compound 8 showing it at highest field. The carbonyl carbons of 6 and 7 are broadened; 6 shows two singlets and 7 shows one singlet in CD_2Cl_2. Changing the NMR solvent to THF-d_8 improved the carbonyl spectra of 6; two doublets (1:3) were observed in this solvent. Changing to THF did not improve the spectrum of 7. With 5, three broadened signals could be seen with relative ratios 1:2:1 as expected for the cis geometry of the complex. The carbonyl resonances in 8 appear as two triplets (1:2) as expected.

The similarities in the ^{13}C spectra of compounds 6–8 in the aryl region allow assignments to be made that are internally consistent. The ipso carbons of the metallacyclic aryl rings in 6–8 [e.g., C(21) in compound 7] appear as doublets in the region δ 143–147 with $J_{PC} \sim 9$ Hz. The ipso carbons on the free aryl rings in 6 appear as a doublet at δ 151.18 as expected based on comparisons with metallacycles studied by Stewart.[15] For example, $CpFe(CO)[P(OPh)_2(o\text{-}OC_6H_4)]$ shows the ipso carbons of the two free aryl rings as two doublets in the region δ 151–152. The other quaternary aryl carbon in the metallacyclic ring of 6 is believed to be in the low-field region also, since the resonances for the analogous carbons in 7 and 8 are clearly there. The upfield singlet in this area for 6–8 (δ 151.12 for 6) is assigned to that type of carbon. The remaining aryl resonances in 6–8 are assigned on the basis of intensity differences as well as chemical shift and coupling constant comparisons. In 6, the meta, para, and ortho carbons of

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Table V. Positional Parameters and Their Estimated Standard Deviations for Compound 7[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mn	0.23666 (3)	0.11143 (2)	0.10836 (6)	2.95 (1)
P1	0.10269 (5)	0.09953 (3)	0.0713 (1)	3.09 (2)
P2	0.37263 (5)	0.10919 (3)	0.1439 (1)	2.93 (2)
O1	0.0436 (1)	0.12338 (9)	0.2112 (3)	3.82 (5)
O2	0.0712 (1)	0.04207 (9)	0.0591 (3)	3.76 (5)
O3	0.0588 (1)	0.11637 (9)	−0.0853 (3)	3.96 (5)
O4	0.3953 (1)	0.06916 (9)	0.2760 (3)	3.72 (5)
O5	0.4331 (1)	0.09160 (9)	−0.0037 (3)	3.45 (5)
O6	0.4249 (1)	0.15853 (9)	0.1883 (3)	3.68 (5)
O10	0.2037 (2)	0.2181 (1)	0.1818 (4)	6.20 (7)
O20	0.2793 (2)	0.1266 (2)	−0.2309 (3)	6.91 (8)
O30	0.2085 (2)	0.0803 (1)	0.4439 (3)	5.31 (7)
C1	0.2194 (2)	0.1767 (1)	0.1530 (5)	4.06 (8)
C2	0.2605 (2)	0.1220 (2)	−0.0998 (4)	4.27 (9)
C3	0.2186 (2)	0.0920 (1)	0.3157 (4)	3.67 (8)
C4	0.2471 (2)	0.0310 (1)	0.0456 (4)	4.01 (8)
C11	−0.0443 (2)	0.1266 (1)	0.2253 (4)	3.47 (8)
C12	−0.0745 (2)	0.1657 (2)	0.3180 (4)	4.28 (9)
C13	−0.1609 (2)	0.1716 (2)	0.3427 (5)	5.2 (1)
C14	−0.2145 (2)	0.1377 (2)	0.2770 (5)	5.1 (1)
C15	−0.1827 (2)	0.0991 (2)	0.1846 (5)	4.87 (9)
C16	−0.0970 (2)	0.0931 (2)	0.1583 (5)	4.44 (9)
C21	0.1053 (2)	0.0064 (1)	0.1613 (4)	3.74 (8)
C22	0.1914 (2)	0.0004 (1)	0.1522 (4)	3.94 (8)
C23	0.2234 (3)	−0.0355 (2)	0.2606 (5)	6.0 (1)
C24	0.1692 (3)	−0.0620 (2)	0.3618 (6)	7.2 (1)
C25	0.0845 (3)	−0.0542 (2)	0.3626 (5)	6.7 (1)
C26	0.0512 (3)	−0.0192 (2)	0.2628 (5)	5.3 (1)
C31	0.0770 (2)	0.1623 (1)	−0.1638 (4)	3.66 (8)
C32	0.0752 (2)	0.2075 (2)	−0.0860 (4)	4.27 (9)
C33	0.0952 (3)	0.2512 (2)	−0.1695 (5)	5.4 (1)
C34	0.1140 (3)	0.2492 (2)	−0.3279 (5)	6.1 (1)
C35	0.1126 (3)	0.2034 (2)	−0.4051 (5)	6.0 (1)
C36	0.0941 (2)	0.1593 (2)	−0.3237 (4)	4.7 (1)
C41	0.4776 (2)	0.0556 (1)	0.3113 (4)	3.28 (7)
C42	0.5091 (2)	0.0111 (1)	0.2519 (4)	4.26 (9)
C43	0.5881 (2)	−0.0045 (2)	0.2931 (5)	4.72 (9)
C44	0.6339 (2)	0.0250 (2)	0.3924 (5)	4.83 (9)
C45	0.6003 (2)	0.0692 (2)	0.4506 (5)	4.85 (9)
C46	0.5213 (2)	0.0847 (2)	0.4106 (4)	4.33 (9)
C51	0.4999 (2)	0.1199 (1)	−0.0732 (4)	3.30 (7)
C52	0.4842 (2)	0.1571 (2)	−0.1786 (5)	4.74 (9)
C53	0.5512 (3)	0.1829 (2)	−0.2496 (5)	6.0 (1)
C54	0.6319 (3)	0.1709 (2)	−0.2164 (5)	5.4 (1)
C55	0.6461 (2)	0.1338 (2)	−0.1120 (5)	5.1 (1)
C56	0.5806 (2)	0.1076 (1)	−0.0377 (5)	4.13 (8)
C61	0.3937 (2)	0.1999 (1)	0.2737 (4)	3.16 (7)
C62	0.4008 (2)	0.2461 (1)	0.2014 (5)	4.12 (8)
C63	0.3745 (3)	0.2885 (2)	0.2836 (6)	5.5 (1)
C64	0.3429 (3)	0.2838 (2)	0.4353 (5)	5.9 (1)
C65	0.3360 (2)	0.2374 (2)	0.5058 (5)	5.6 (1)
C66	0.3620 (2)	0.1943 (2)	0.4257 (4)	4.29 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

the free aryl rings are at δ 130.29, 125.94, and 121.67, respectively, whereas the four methine carbons of the metallacyclic rings are less intense singlets at δ 127.08, 125.53, 124.72, and 119.47. For 7 and 8, the most intense resonances are for the meta and ortho carbons of the aryl rings in the $P(OPh)_3$ ligand; these are at δ 130.15, 121.41 and 130.25, 121.47, respectively. The meta and ortho carbons in the aryl rings of the $P(OPh)_2$ group are less intense and appear at δ 129.98, 121.70 and 130.07, 121.72 for 7 and 8, respectively. The para carbons of the $P(OPh)_3$ and $P(OPh)_2$ units in both compounds are coincident at δ 125.35 and 125.46 for 7 and 8, respectively. The remaining four aryl carbons of the metallacyclic ring in each case appear as low-intensity signals (δ 127.06, 124.68, 124.06, and 119.08 for 7; δ 126.77, 124.40, 123.61, and 120.14 for 8). The aryl carbon resonances for 5 span a broad range (δ 125–161). The lowest field signal is a doublet (J = 36.1 Hz) and is assigned to the quaternary carbon C(12); low-field resonances with substantial J_{PC} values seem to be characteristic of this type of metallacyclic carbon.[7,16] The ipso carbons appear as two doublets of unequal intensity; the higher intensity doublet (at δ 135.76) is assigned to the ipso carbons of the two free aryl rings, and the other one (at δ 135.67) is assigned to C(11). The resonances at δ 133.10, 131.32, and 129.63 are assigned to the ortho, para, and meta carbons, respectively, of the free aryl rings. The remaining resonances are of lower intensity and are assigned to the four methine carbons of the metallacyclic ring. Although unequivocal assignments for each carbon cannot be made, we suggest that the singlet at δ 130.03 is due to C(14), which is para to phosphorus, and that C(16) is the doublet at δ 130.83. The other two doublets (δ 131.15 and 125.73) show smaller coupling constants and are assigned to C(13) and C(15), which are meta to the phosphorus atom. The chemical shift positions of the aryl carbons in 5 are comparable to those in the rhenium complex reported by Gladysz[3] (coupling constant data were not reported).

Hydrogen Halide Cleavage of Metallacycles 7 and 8. Although metallacycles 5–8 are prepared under strongly acidic conditions with either trifluoroacetic acid or HBF_4·etherate, the metal–carbon σ bond in each compound is stable under the conditions of the synthesis. However, ring opening of 7 and 8 occurred readily upon treatment with HBr in CH_2Cl_2 to give *mer,trans*-$M(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_3)]Br$ (M = Mn, Re). Both products were formed in nearly quantitative yields and have been characterized by elemental analyses and by IR, ^1H NMR, and ^{13}C NMR spectroscopy (see Experimetal Section). The lability toward hydrogen halides of similar metal–carbon σ bonds in related five-membered metallacyclic compounds has been demonstrated previously.[7,17]

Metallacycle 8 can also be prepared by thermolysis of *mer,trans*-$Re(CO)_3[P(OPh)_3]_2CH_2I$[11] in the presence of a hindered base (see Experimental Section). In the absence of base, thermolysis of the iodomethyl complex yields a product whose spectral properties are closely similar to the ring-opened bromide described above and indicate that it is *mer,trans*-$Re(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_3)]I$; HI liberated in the thermolysis of the iodomethyl complex is apparently sufficient to cleave the metallacycle.

Experimental Section

General Data. Reagent-grade acetonitrile was dried over type 3A molecular sieves. Hexanes and pentane were dried over concentrated H_2SO_4 and fractionally distilled. Reagent grade anhydrous ether and dichloromethane were used as received. Spectroscopic measurements were obtained on the following instruments: ^1H NMR, Varian XL-300, EM-390, and T-60; ^{13}C and ^{31}P NMR, Varian XL-300; IR, Perkin-Elmer 599B. ^1H and ^{13}C NMR chemical shifts were referenced to tetramethylsilane. ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4 and reported in parts per million downfield (+). Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Trifluoroacetic acid, 2,4,6-trimethylpyridine, $HBF_4 \cdot Me_2O$, CD_2Cl_2, THF-d_8, and acetone-d_6 were obtained from Aldrich and used directly. All reactions were performed under an atmosphere of prepurified nitrogen.

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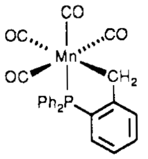
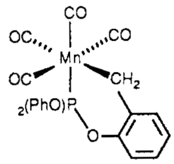
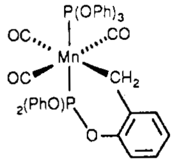
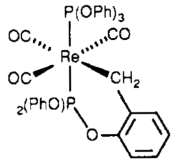
(16) (a) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 238. (b) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1051.

(17) Carriedo, G. A.; Parra Soto, J. B.; Riera, V.; Solans, X.; Miravitlles, C. *J. Organomet. Chem.* **1985**, *297*, 193.

Table VI. ^{1}H and ^{13}C NMR Data for Metallacycles

	^{1}H NMR,[a] δ		^{13}C NMR,[a] δ		
compd	phenyl	methylene	CO	phenyl	methylene
	7.50[b] (m, 14 H)	2.60 (d, J_{PH} = 3.0 Hz, 2 H)	219.87 (br, s, 1 CO),[c] 218.94 (br, s, 2 CO), 217.37 (br, s, 1 CO)	161.10 (d, J_{PC} = 36.1 Hz), 135.76 (d, J_{PC} = 42.8 Hz), 135.67 (d, J_{PC} = 49.9 Hz), 133.10 (d, J_{PC} = 11.0 Hz), 132.03 (s), 131.32 (s), 131.15 (d, J_{PC} = 2.3 Hz), 130.83 (d, J_{PC} = 14.6 Hz), 129.63 (d, J_{PC} = 9.8 Hz), 125.73 (d, J_{PC} = 6.3 Hz)	18.10 (d, J_{PC} = 7.3 Hz)
	7.20 (m, 14 H)	2.00 (d, J_{PH} = 13.2 Hz, 2 H)	218.3 (br, s, 1 CO),[d] 213.5 (br, s, 3 CO)	151.18 (d, J_{PC} = 9.5 Hz), 151.12 (s), 142.76 (d, J_{PC} = 8.6 Hz), 130.29 (s), 127.08 (s), 125.94 (s), 125.53 (s), 124.72 (s), 121.67 (d, J_{PC} = 3.9 Hz), 119.47 (s)	2.39 (d, J_{PC} = 21.9 Hz)
	7.08 (m, 29 H)	2.12 (dd, J_{PH} = 12.1, 9.4 Hz, 2 H)	215.87 (br, m)	151.92 (d, J_{PC} = 10.6 Hz), 151.53 (d, J_{PC} = 10.6 Hz), 151.14 (s), 143.82 (d, J_{PC} = 9.1 Hz), 130.15 (s), 129.98 (s), 127.06 (s), 125.35 (s), 124.68 (s), 124.06 (s), 121.70 (d, J_{PC} = 3.7 Hz), 121.41 (s), 119.08 (s)	3.81 (dd, J_{PC} = 21.6, 17.0 Hz)
	7.32 (m, 29 H)	2.15 (dd, J_{PH} = 11.9, 8.2 Hz, 2 H)	190.08 (t, J_{PC} = 13.7 Hz, 2 CO), 187.94 (t, J_{PC} = 7.2 Hz, 1 CO)	151.75 (d, J_{PC} = 8.4 Hz), 151.49 (d, J_{PC} = 8.9 Hz), 150.51 (s), 146.58 (d, J_{PC} = 7.0 Hz), 130.25 (s), 130.07 (s), 126.77 (s), 125.46 (s), 124.40 (s), 123.61 (s), 121.72 (d, J_{PC} = 4.7 Hz), 121.47 (d, J_{PC} = 4.6 Hz), 120.14 (d, J_{PC} = 4.3 Hz)	−8.55 (dd, J_{PC} = 10.6, 8.9 Hz)

[a] CD_2Cl_2 unless otherwise noted. [b] Acetone-d_6. [c] THF-d_8. [d] In THF-d_8 at 19 °C, both carbonyl signals appear as doublets [218.89 (d, J_{PC} = 28.6 Hz) and 213.78 (d, J_{PC} = 26.6 Hz)].

***cis*-$\mathbf{Mn(CO)_4[P(Ph)_2(\textit{o}\text{-}C_6H_4CH_2)]}$ (5) from $\mathbf{HBF_4{\cdot}Me_2O}$.** To a CH_2Cl_2 solution (20 mL) containing $HBF_4{\cdot}Me_2O$ (0.050 g, 0.37 mmol) at 0 °C was added *cis*-$Mn(CO)_4(PPh_3)CHO$[10] (0.115 g, 0.25 mmol) with stirring. After 10 min, when the reaction was over, the solvent was removed on a rotary evaporator, leaving an off-white residue. The residue was extracted with 3 × 5 mL of hexanes; the combined extracts were evaporated to dryness giving 0.41 g (74% yield) of the product as an off-white powder, mp 127.5–128 °C.

Anal. Calcd for $C_{23}H_{16}O_4PMn$: C, 62.46; H, 3.65; P, 7.00. Found: C, 62.25; H, 4.02; P, 7.18. IR ν_{CO} (hexanes) 2060 (m), 1980 (s), 1970 (vs), and 1940 (s) cm^{-1}; $^{31}P[^1H]$ NMR (acetone-d_6) 77.65 (s); the other NMR spectral properties of the metallacycle are summarized in Table VI.

The insoluble residue was dissolved in CH_2Cl_2 (10 mL), mixed with diethyl ether (10mL), and cooled to −20 °C to achieve precipitation. The pale yellow solid that formed was then collected by filtration and dried, giving 0.062 g (92% yield) of a product whose spectral properties were identical with those of an authentic sample of $Mn(CO)_5(PPh_3)^+BF_4^-$.[10]

***cis*-$\mathbf{Mn(CO)_4[P(Ph)_2(\textit{o}\text{-}C_6H_4CH_2)]}$ (5) from $\mathbf{CF_3COOH}$.** To a CH_2Cl_2 solution (20 mL) containing CF_3COOH (0.228 g, 2.00 mmol) at −78 °C was added *cis*-$Mn(CO)_4(PPh_3)CHO$[10] (0.460 g, 1.00 mmol) with stirring. After 5 min, the dry ice bath was removed, and the mixture was allowed to warm slowly to room temperature over 1 h. The solvent was removed on a rotary evaporator, giving a pale yellow residue. The residue was extracted with 3 × 10 mL of hexanes; the extracts were concentrated to 5 mL and chilled to −20 °C. The precipitated product was collected by filtration, and the filtrate was kept aside. Recrystallization of the precipitate from hexanes gave 0.121 g (44% yield) of *cis*-$Mn(CO)_4(PPh_3)CH_2OC(O)CF_3$, mp 99–99.5 °C.

Anal. Calcd for $C_{25}H_{17}F_3O_6PMn$: C, 53.98; H, 3.09; P, 5.57. Found: C, 54.23; H, 2.87; P, 5.70. IR ν_{CO} (hexanes) 2070 (m), 2000 (s), 1977 (vs), 1950 (s), and 1770 (m) cm^{-1}; ^{1}H NMR (acetone-d_6) 7.60 (m, 15 H), 4.52 (d, J_{PH} = 6.0 Hz, 2 H); ^{13}C NMR (CD_2Cl_2) 216.20 (d, J_{PC} = 21.7 Hz), 214.80 (d, J_{PC} = 8.7 Hz), 214.50 (d, J_{PC} = 14.6 Hz), 158.00 (q, J_{CF} = 41.0 Hz), 132.75 (d, J_{PC} = 7.5 Hz), 132.08 (d, J_{PC} = 41.5 Hz), 130.00 (s), 128.70 (d, J_{PC} = 7.5 Hz), 114.50 (q, J_{CF} = 285.0 Hz), 68.10 (d, J_{PC} = 9.6 Hz); $^{31}P[^1H]$ NMR (acetone-d_6) 59.4 (s).

The filtrate from above was chromatographed on a short Florisil column (60–120 mesh); elution with CH_2Cl_2/hexanes (20 mL, 1:1) afforded a pale yellow solution of the metallacycle *cis*-$Mn(CO)_4[P(Ph)_2(o\text{-}C_6H_4CH_2)]$. After removal of the solvent mixture on a rotary evaporator under reduced pressure, the metallacycle was obtained as an off-white powder, 0.102 g (46% yield). The spectral properties of this product were identical with those of the product obtained from the procedure above.

Next, the column was eluted with CH_2Cl_2 (25 mL) to give a yellow solution from which the solvent was removed on a rotary evaporator under reduced pressure to yield a very small amount of *cis*-$Mn(CO)_4(PPh_3)O_2CCF_3$ as a yellow solid; IR ν_{CO} (hexanes) 2098 (s), 2031 (s), 2009 (vs), 1958 (s), and 1686 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.5 (m); $^{31}P[^1H]$ NMR (C_6D_6) 45.0 (s) [lit.[18] IR ν_{CO} 2098 (s), 2033 (s), 2011 (s), 1960 (s), and 1678 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.5 (s)].

The insoluble part from above was dissolved in CH_2Cl_2 (5 mL), mixed with hexanes (1 mL), and chilled at −20 °C to precipitate the salt $Mn(CO)_5(PPh_3)^+O_2CCF_3^-$ as a pale yellow solid. The product was collected by filtration to give 0.254 g (90% yield) of product; IR ν_{CO} (CH_2Cl_2) 2140 (m), 2070 (sh), and 2050 (vs) cm^{-1} [lit.[10] IR for $Mn(CO)_5(PPh_3)^+BF_4^-$ 2140 (m), 2090 (sh), 2070 (sh), and 2050 (vs) cm^{-1}].

***cis*-$\mathbf{Mn(CO)_4[P(OPh)_2(\textit{o}\text{-}OC_6H_4CH_2)]}$ (6).** The formyl compound *cis*-$Mn(CO)_4[P(OPh)_3]CHO$ was generated in solution by using 0.400 g of $Mn(CO)_5[P(OPh)_3]^+BF_4^-$ as described previously.[10] To this reaction mixture, maintained at −40 °C, was added 4 mL of CF_3COOH; after 10 min, the mixture was allowed to warm to room temperature. The solvent was removed by a rotary evaporator, and the residue triturated with 3 × 20 mL of hexanes. The extracts were combined, and the volume of the solvent was reduced to 5 mL; the product was purified by chromatography on a short alumina column with elution by hexanes. The solvent was removed from the product by a rotary evaporator to leave an oily yellow residue. The residue was taken up in CH_2Cl_2, dried over anhydrous $MgSO_4$, and filtered through Celite. The CH_2Cl_2 solution was concentrated to a small volume, hexanes

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[18] Bannister, W. D.; Booth, B. L.; Haszeldine, R. N.; Loader, P. L. *J. Chem. Soc. A* **1971**, 930.

were added (to the cloud point), and the solution was chilled to −30 °C to give the metallacycle as small yellow needles, 0.15 g (82% yield), mp 86–89 °C.

Anal. Calcd for $C_{23}H_{16}O_7PMn$: C, 56.34; H, 3.29; P, 6.32. Found: C, 56.01; H, 3.52; P, 6.41. IR ν_{CO} (CH_2Cl_2) 2080 (m), 1995 (s), 1985 (vs), and 1960 (s) cm^{-1}. See Table VI for the NMR spectral properties.

The insoluble residue from above was identified as $Mn(CO)_5[P(OPh)_3]^+O_2CCF_3^-$ from its IR spectrum: ν_{CO} (CH_2Cl_2) 2160 (w) and 2070 (vs) cm^{-1} [lit.[10] IR for $Mn(CO)_5[P(OPh)_3]^+BF_4^-$ 2160 (w), 2095 (sh) and 2070 (vs) cm^{-1}]. Attempts to purify the $Mn(CO)_5[P(OPh)_3]^+O_2CCF_3^-$ resulted in its decomposition.

***mer,trans*-$\mathbf{Mn(CO)_3[P(OPh)_3][P(OPh)_2(\mathit{o}\text{-}OC_6H_4CH_2)]}$ (7).** To a stirred solution of 3 mL CF_3COOH in 3 mL of CH_3CN maintained at 0 °C was added 0.34 g (0.43 mmol) of *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CHO$[10] in four small portions. Each portion was allowed to dissolve before the next was added. The total elapsed time for the additions was about 1 min. The reaction mixture was then allowed to warm to room temperature over approximately 20 min; solvent was then evaporated on a rotary evaporator, and the residue triturated with 3 × 20 mL of hexanes. The extracts were combined and the solvent was evaporated to give an oily yellow residue, which was taken up in CH_2Cl_2/hexanes and chilled to give the metallacycle as small yellow needles, 0.10 g (60% yield), mp 108.5–110 °C.

Anal. Calcd for $C_{40}H_{31}O_9P_2Mn$: C, 62.19; H, 4.05; P, 8.02. Found: C, 61.83; H, 4.14; P, 7.96. IR ν_{CO} (CH_2Cl_2) 2040 (w), 1960 (s), and 1935 (m) cm^{-1}. See Table VI for the NMR spectral properties.

The insoluble residue from above was dissolved in CH_2Cl_2 and washed with 3 × 10 mL of water. The CH_2Cl_2 layer was dried over anhydrous $MgSO_4$, filtered through celite, and the solvent evaporated. The residue was recrystallized from CH_2Cl_2 and hexanes to give the salt *trans*-$Mn(CO)_4[P(OPh)_3]_2^+O_2CCF_3^-$ as small white needles, 0.12 g (60% yield); IR ν_{CO} (CH_2Cl_2) 2115 (w), 2070 (vw), and 2040 (vs) cm^{-1} [lit.[10] IR for the related cation *trans*-$Mn(CO)_4[P(OPh)_3]_2^+BF_4^-$ 2115 (vw), 2070 (w), and 2040 (s) cm^{-1}].

***mer,trans*-$\mathbf{Re(CO)_3[P(OPh)_3][P(OPh)_2(\mathit{o}\text{-}OC_6H_4CH_2)]}$ (8). Method A.** To a mixture of 5 ml of CH_2Cl_2 and 3 mL of CF_3COOH, stirred and maintained at −78 °C, was added (0.159 g, 0.173 mmol) *mer,trans*-$Re(CO)_3[P(OPh)_3]_2CHO$.[10] After an hour, the solvent was removed under vacuum at room temperature. The residue was dried under vacuum for 1 h and then extracted with 3 × 20 mL of hexanes. The extracts were combined, and the solvent was removed on a rotary evaporator (water bath maintained at room temperature). The oily residue was dissolved in ether, and the solvent was treated with anhydrous $MgSO_4$ and filtered through Celite. The ether solution was concentrated to 2 mL on a rotary evaporator (again maintaining the water bath at room temperature), 10 mL of hexanes was added, and the solution was then chilled to −30 °C. The white crystalline product that formed over 1 week was collected by filtration and dried, in vacuo, to give 0.072 g (92% yield), mp 109–111 °C.

Anal. Calcd for $C_{40}H_{31}O_9P_2Re$: C, 53.16; H, 3.46; P, 6.85. Found: C, 53.24; H, 3.60; P, 6.49. IR ν_{CO} (CH_2Cl_2) 2060 (w), 1965 (s), and 1930 (m) cm^{-1}. See Table VI for the NMR spectral properties.

The hexane-insoluble residue from the extraction above was washed with 3 × 20 mL of water and then dissolved in CH_2Cl_2. This solution was dried over anhydrous $MgSO_4$, treated with activated charcoal, and filtered through Celite. The filtrate was concentrated to 3 mL on a rotary evaporator, and then 20 mL of anhydrous ether was added. Upon chilling for 2 days at −30 °C, *trans*-$Re(CO)_4[P(OPh)_3]_2^+O_2CCF_3^-$ was obtained as white crystals, 0.048 g (54% yield); IR ν_{CO} (CH_2Cl_2) 2080 (w) and 2038 (s) cm^{-1} [lit.[10] IR *trans*-$Re(CO)_4[P(OPh)_3]_2^+BF_4^-$, same].

Method B. *mer,trans*-$Re(CO)_3[P(OPh)_3]_2CH_2I$[11] (0.206 g, 0.199 mmol) was dissolved in 5 mL of CH_2Cl_2 maintained at 0 °C. 2,4,6-Trimethylpyridine (26.5 μL, 0.200 mmol) was added, and the solution was allowed to warm to room temperature. After being stirred at room temperature for 12 h, the solution was concentrated to 2 mL, and then 20 mL of anhydrous ether was added. The mixture was filtered through Celite to remove the precipitated pyridinium iodide, and solvent was removed from the filtrate on a rotary evaporator. The residual oil was dissolved in anhydrous ether and then dried over $MgSO_4$; the solution was decanted, treated with activated charcoal, and then filtered through Celite. The filtrate was concentrated to 2 mL, 10 mL of hexanes was added, and the solution was chilled to −30 °C. White crystals of the metallacycle formed slowly, during about 1 week (0.164 g, 91%); the product was identical with that formed by method A.

***mer,trans*-$\mathbf{Mn(CO)_3[P(OPh)_3][P(OPh)_2(\mathit{o}\text{-}OC_6H_4CH_3)]Br}$.** HBr gas was bubbled through 3 mL of CH_2Cl_2 for 20 s; the resulting solution was added to a stirred solution of metallacycle 7 (0.100 g, 0.129 mmol) in 5 mL of CH_2Cl_2. After 10 min, solvent was removed on a rotary evaporator at room temperature; the residue was dissolved in CH_2Cl_2, dried over $MgSO_4$, treated with activated charcoal, and then filtered through Celite. The filtrate was concentrated to 2 mL; 12 mL of pentane was added, and the solution was chilled to −30 °C. After 1 day, orange crystals of the product were collected and dried, in vacuo (0.100g, 91% yield), mp 143–145 °C (dec).

Anal. Calcd for $C_{40}H_{32}O_9P_2MnBr$: C, 56.29; H, 3.81; Br, 9.36. Found: C, 55.90; H, 3.85; Br, 9.32. IR ν_{CO} (CH_2Cl_2) 2070 (vw), 1990 (s), and 1950 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) 7.29 (m) and 2.28 (s); $^{13}C[^1H]$ NMR (CD_2Cl_2) 217.40 (br, s), 212.31 (br, s), 151.78 (dd, J_{PC} = 2.8 and 8.0 Hz), 150.62 (dd, J_{PC} = 2.6 and 7.2 Hz), 132.05 (s), 130.65 (s), 130.04 (s), 129.93 (s), 127.25 (s), 125.56 (s), 125.46 (s), 121.67 (d, J_{PC} = 2.3 Hz), 121.50 (d, J_{PC} = 2.4 Hz), 120.28 (s), and 17.02 (s). The proton-coupled spectrum shows this latter resonance as a quartet of doublets (J_{PC} = 127.7 and 5.3 Hz).

***mer,trans*-$\mathbf{Re(CO)_3[P(OPh)_3][P(OPh)_2(\mathit{o}\text{-}OC_6H_4CH_3)]Br}$.** HBr gas was bubbled through 3 mL of CH_2Cl_2 for 1 min; the resulting solution was added to a stirred solution of metallacycle 8 (0.104 g, 0.115 mmol) in 5 mL of CH_2Cl_2. After 10 min, solvent was removed on a rotary evaporator at room temperature; the residue was dissolved in CH_2Cl_2, dried over $MgSO_4$, treated with activated charcoal, and then filtered through Celite. The filtrate was concentrated to 3 mL, 20 mL of hexanes was added, and the solution was chilled to −30 °C. After 2 days, white crystals of the product were collected and dried in vacuo (0.106 g, 94%), mp 159–160 °C (dec).

Anal. Calcd for $C_{40}H_{32}O_9P_2ReBr$: C, 48.79; H, 3.27; Br, 8.11. Found: C, 48.62; H, 3.26; Br, 8.08. IR ν_{CO} (CH_2Cl_2) 2080 (w), 1995 (s), and 1933 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) 7.23 (m) and 2.24 (s); $^{13}C[^1H]$ NMR (CD_2Cl_2) 186.35 (t, J_{PC} = 13.5 Hz), 183.52 (t, J_{PC} = 10.2 Hz), 151.47 (m), 150.43 (m), 132.05 (s), 130.68 (s), 130.16 (s), 130.08 (s), 127.30 (s), 125.68 (s), 125.51 (s), 121.78 (s), 121.61 (s), 120.47 (s), and 17.00 (s); the proton-coupled carbon NMR spectrum shows this latter resonance as a quartet of doublets (J_{CH} = 128.1 and 5.0 Hz).

X-ray Crystal Structure of 5. A suitable single crystal was grown by layering a CH_2Cl_2 solution of the metallacycle with hexanes. Data were collected on an Enraf-Nonius CAD4 diffractometer as outlined in Table I. Of 3695 unique reflections, 2842 had $I > 3\sigma(I)$. The manganese position was obtained from a three-dimensional Patterson map. Several cycles of Fourier synthesis and full-matrix least-squares refinement yielded positions of all non-hydrogen atoms. The positions of the metallacyclic hydrogen atoms were located from a difference Fourier map and included in these positions. All non-hydrogen atoms were refined with anisotropic thermal parameters while the other atomic positions and thermal parameters were kept constant. A final R index of 0.029 with R_w = 0.033 was obtained for 263 variables. The temperature factors of the hydrogen atoms were set to 1.1 times the temperature factors of the carbons to which they were bonded.

X-ray Crystal Structure of 7. A suitable single crystal was grown from CH_2Cl_2 and hexanes. Data were collected on a CAD4 diffractometer as outlined in Table I. Of 4715 unique reflections, 3547 had $I > 3\sigma(I)$. The manganese position was obtained from a three-dimensional Patterson map. Several cycles of Fourier synthesis and least-squares refinement yielded positions of all non-hydrogen atoms. The positions of the metallacyclic hydrogen atoms were located from a difference Fourier map and included in these positions. All non-hydrogen atoms were refined with anisotropic thermal parameters, while the other atomic positions and thermal parameters were kept constant. A final R index of 0.039 with R_w = 0.049 was obtained for 470 variables. The temperature factors of the hydrogen atoms were set to 1.3 times the temperature factors of the carbons to which they were bonded.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, bond distances, and bond angles for 5 and 7 (14 pages); tables of structure factor amplitudes for 5 and 7 (23 pages). Ordering information is given on any current masthead page.

Regiospecific Condensation of Methyl Propiolate with 2,3-Dimethyl-2-butene Mediated by the Electrophilic η^5-Cyclopentadienyl Dinitrosyl Tetrafluoroborate Salts of the Group 6 Metals[1,2]

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Chloride abstraction from $\mathrm{Cp'M(NO)_2Cl}$ (Cp′ = Cp (η^5-$\mathrm{C_5H_5}$), Cp* (η^5-$\mathrm{C_5Me_5}$); M = Cr, Mo, W) with an equimolar amount of $\mathrm{AgBF_4}$ in $\mathrm{CH_2Cl_2}$ generates reactive solutions of $\mathrm{Cp'M(NO)_2BF_4}$. During their reactions with various nucleophiles, the $\mathrm{Cp'M(NO)_2BF_4}$ compounds behave as though they are the formally 16-electron cations $\mathrm{Cp'M(NO)_2}^+$. Thus, all the $\mathrm{CpM(NO)_2BF_4}$ complexes abstract a phenyl group from the $\mathrm{BPh_4}^-$ anion to form the known $\mathrm{CpM(NO)_2Ph}$ compounds, and $\mathrm{CpW(NO)_2BF_4}$ catalyzes the oligomerization of 2-methylpropene. Furthermore, methyl propiolate and 2,3-dimethyl-2-butene condense regiospecifically in the coordination spheres of all the $\mathrm{Cp'M(NO)_2}^+$ cations to produce the cationic lactone complexes $[\mathrm{Cp'M(NO)_2}\overline{\mathrm{C{=}C(H)C(Me)_2C(Me)_2OC}}\mathrm{(OMe)}]^+$. All the cationic lactone complexes undergo facile *O*-demethylation reactions upon exposure to an acetone solution of NaI. The resulting η^1-lactone-containing organometallic compounds, $\mathrm{Cp'M(NO)_2}\overline{\mathrm{C{=}C(H)C(Me)_2C(Me)_2OC}}\mathrm{({=}O)}$, have all been fully characterized by conventional spectroscopic techniques, and a single-crystal X-ray crystallographic analysis has been performed on the CpMo member of this series of complexes. Crystal data for $\mathrm{CpMo(NO)_2}\overline{\mathrm{C{=}C(H)C(Me)_2C(Me)_2OC}}\mathrm{({=}O)}$: a = 11.337 (6) Å, b = 12.564 (3) Å, c = 11.958 (6) Å, β = 115.12 (4)°, Z = 4, space group $P2_1/c$, number of unique reflections 2713, number of variables 245, R_F = 0.021, R_{wF} = 0.030. The compound possesses a normal three-legged piano-stool molecular geometry, the intramolecular dimensions of the lactone ligand indicating the existence of some internal delocalization of π-electron density. Treatment of the neutral CpMo lactone complex with $\mathrm{[Me_3O]BF_4}$ regenerates its cationic organometallic precursor, and treatment with iodine liberates the iodolactone from the molybdenum's coordination sphere. Interestingly, exposure of the neutral tungsten lactone complexes to air results in their being cleanly converted to the corresponding dioxo derivates $\mathrm{Cp'W(O)_2}$(η^1-lactone).

Introduction

Transition-metal organometallic compounds continue to be widely exploited for effecting various specific organic transformations.[5] A principal reason for this state of affairs is that many catalytic and stoichiometric reactions resulting in the production of new organic compounds proceed only in the presence of a reactive organometallic fragment.[6] The large majority of the organometallic fragments employed during such reactions have involved carbonyl-containing species.[6] In principle, the related nitrosyl complexes should also be capable of functioning as specific reactants or selective catalysts for various organic conversions. However, the synthetic utility of these latter species has to date been relatively little exploited despite the fact that there is now a considerable number of organometallic nitrosyl complexes available.[7] One of the main differences between the two types of compounds is that the presence of the more electron-withdrawing NO

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