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Formation and Molecular Structure of Hydridotricarbonyl{[η^5-(diphenylphosphino)cyclopentadienyl][η^7-(diphenylphosphino)cycloheptatrienyl]titanium-*P*,*P'*}manganese: A New Chelated Titanium–Manganese Heterobimetallic Compound

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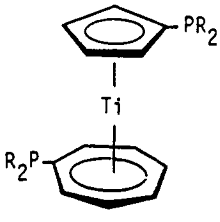
A reaction between $Mn_2(CO)_{10}$ and 2 equiv of $(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti$ (1) in refluxing toluene results in carbonyl group displacement, metal–metal bond cleavage, and hydrogen abstraction to form $HMn(CO)_3[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]$ (4) in 57% yield. The new chelated heterobimetallic compound 4 has been characterized by its ^1H NMR, ^{31}P NMR, IR, and mass spectra, as well as by a single-crystal X-ray diffraction study. Compound 4 crystallizes in the triclinic space group $P\bar{1}$ with (at 20 °C) $a = 10.135$ (4) Å, $b = 10.366$ (4) Å, $c = 18.484$ (4) Å, $\alpha = 102.80$ (3)°, $\beta = 93.60$ (3)°, $\gamma = 116.42$ (4)°, $D_{calcd} = 1.42$ g cm^{-3} for $Z = 2$, and $R = 0.061$ based on 1981 observed $[F_o \geq 5\sigma(F_o)]$ reflections. The manganese atom exhibits a distorted octahedral geometry with *cis*-phosphines. One carbonyl is trans to the hydride position. The titanium backbone is relatively unaffected by coordination.

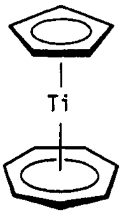
Introduction

Recent studies in our laboratory have demonstrated that the bis(phosphine) compounds $(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti$ (1)[1] and $(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti$ (2)[2] can be prepared in high yields by the dimetalation of the mixed-sandwich compound $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ (3), followed by reactions with either Ph_2PCl or Me_2PCl, respectively. Compounds 1 and 2 undergo reactions with various metal carbonyls of Cr, Mo, Fe, and Co, leading to chelated heterobimetallic complexes in which 1 or 2 function as bis(phosphine) ligands and displace two molecules of carbon monoxide from the metal.[1,2] In this paper, we report the results of synthetic and structural studies on reactions of 1 with $Mn_2(CO)_{10}$.



1 R = Ph

2 R = Me



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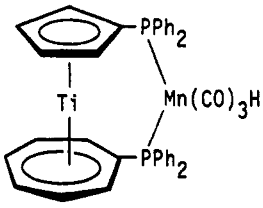
Results and Discussion

Reactions of $Mn_2(CO)_{10}$ with bidentate ligands have been extensively investigated and lead to a variety of substitution products.[3] In particular, we reasoned that a reaction between 2 equiv of 1 and $Mn_2(CO)_{10}$ in refluxing toluene would lead to species of the type $Mn_2(CO)_6(L\frown L)_2$, where $L\frown L$ = 1, a Mn–Mn bond is maintained, and the $L\frown L$ ligands either bridge the two manganese atoms or are separately cis-coordinated to each metal center. Reimann and Singleton[4] have previously shown that the latter type of products result from reactions between $Mn_2(CO)_{10}$ and an excess of either bis(diphenylphosphino)ethane (DPPE) or -methane (DPPM).

In our studies, a reaction between 2 equiv of 1 and $Mn_2(CO)_{10}$ in refluxing toluene, followed by column chromatography and crystallization, produced a diamagnetic blue-green crystalline solid. We initially assumed that this product had the formula $Mn_2(CO)_6[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]_2$, since combustion analyses were consistent for such a composition, three strong bands were observed in the terminal metal carbonyl region as were also observed for $Mn_2(CO)_6(DPPE)_2$[4] and $Mn_2(CO)_6(DPPM)_2$,[4] and an EI mass spectral analysis indicated a peak that could be assigned to $m/e = (M/2 + H)^+$.

Meanwhile, a concurrent X-ray structural investigation of the product clearly indicated that *no* manganese–manganese bond was present but that each manganese atom was indeed bonded to three carbon monoxide ligands as well as to the two phosphorus nuclei of a molecule of 1 (vide infra). This finding thus strongly suggested that the reaction product might have the alternative formula $HMn(CO)_3[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]$ (4).



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† On sabbatical leave from the Corporate Research Institute, Sekisui Chemical Co., Ltd., Osaka, Japan, 1987–1988.

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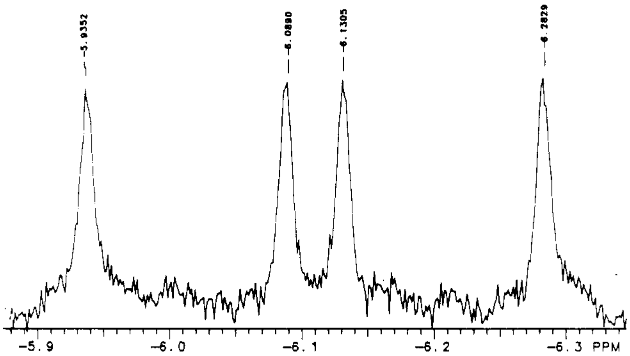

Figure 1. ^1H NMR spectrum of $HMn(CO)_3[(\eta^5$-$C_5H_4PPh_2)(\eta^7$-$C_7H_6PPh_2)Ti]$ (4) in $CDCl_3$ solution in the metal hydride region.

Reactions of $Mn_2(CO)_{10}$ and monodentate phosphine and phosphite ligands in high-boiling solvents have previously been shown to generate compounds of the type $HMn(CO)_3L_2$ under similar conditions.[5-7] The 17-electron radical species $Mn(CO)_3L_2$ are presumed to be intermediates in these reactions and can abstract hydrogen from the solvent to form the hydride product.[3,5]

Reexamination of the IR, NMR, and mass spectra of our reaction product provided further evidence for its formulation as 4. In addition to the three strong terminal metal carbonyl bands, a weak but discernible absorption was noted at 1727 cm^{-1}, which can be assigned to a metal hydride frequency. For comparison, the IR spectrum of $HMn(CO)_5$ contains a weak band at 1783 cm^{-1}, which has been assigned to ν(Mn-H).[3,8]

When we recorded the ^1H NMR spectrum of our product at higher field, an additional resonance was observed as a doublet of doublets centered at δ -6.11 ppm (J_{P-H} = 58.3 and 45.8 Hz) (Figure 1). Such a result is consistent with a highly shielded metal hydride resonance in which spin-spin coupling with the two nonequivalent phosphorus nuclei of chelated 1 is observed. Comparative values for δ(Mn-H) of structurally related compounds include the following: $HMn(CO)_5$, -7.5 ppm (s);[3,8] $HMn(CO)_3(Ph_3P)_2$, -7.4 ppm (t, J_{P-H} = 29 ± 6 Hz);[5] $HMn(CO)_3(PMePh_2)_2$, -7.38 ppm (t, J_{P-H} = 33 Hz).[6,7]

The ^{31}P NMR spectrum of 4 exhibited two resonances that appeared as doublets (J_{P-P} = 46.0 Hz) at δ 64.0 and 89.4 ppm. These results are consistent with the postulate that both nonequivalent diphenylphosphino groups in 4 are coordinated to the same metal atom, as has been previously demonstrated for other heterobimetallic complexes in this series.[1,2]

In the EI mass spectrum of 4, the peak at highest *m/e* value of 712 can be correctly assigned to M^+, and major fragmentation peaks at *m/e* 628 and 572 are attributable to $(M - 3CO)^+$ and $(M - Mn(CO)_3H)^+$ ions, respectively.

X-ray Crystallographic Studies. An ORTEP illustration of 4 is presented in Figure 2, with bond distances and angles in Table I. The $[(\eta^5$-$C_5H_4PPh_2)(\eta^7$-$C_7H_6PPh_2)Ti]$ backbone is bonded to a $HMn(CO)_3$ fragment via the chelating phosphine groups. The phosphines rearrange from a trans orientation in the parent titanium complex (1)[1] to the nearly eclipsed conformation observed in the title complex 4, $[(\eta^5$-$C_5H_4PPh_2)(\eta^7$-$C_7H_6PPh_2)Ti][Cr(CO)_4]\cdot{}^1/_2C_6H_5Me$ (5),[1] and $[(\eta^5$-$C_5H_4PMe_2)(\eta^7$-$C_7H_6PMe_2)Ti][Cr(CO)_4]$ (6).[2] The twist as measured by the P-C(C_7)-C(C_5)-P torsion angle is -36° in 4, 36° in 5, and 38° in 6.

Table I. Bond Distances (Å) and Angles (deg) for $HMn(CO)_3[(\eta^5$-$C_5H_4PPh_2)(\eta^7$-$C_7H_6PPh_2)Ti]$ (4)

Mn(1)-P(1)	2.349 (4)	Mn(1)-P(2)	2.330 (3)
Mn(1)-C(1)	1.81 (2)	Mn(1)-C(2)	1.78 (1)
Mn(1)-C(3)	1.81 (2)	Ti(1)-C(4)	2.17 (1)
Ti(1)-C(5)	2.16 (2)	Ti(1)-C(6)	2.19 (2)
Ti(1)-C(7)	2.23 (1)	Ti(1)-C(8)	2.21 (2)
Ti(1)-C(9)	2.21 (1)	Ti(1)-C(10)	2.18 (1)
Ti(1)-C(11)	2.29 (1)	Ti(1)-C(12)	2.29 (1)
Ti(1)-C(13)	2.30 (1)	Ti(1)-C(14)	2.32 (2)
Ti(1)-C(15)	2.32 (1)	P(1)-C(4)	1.85 (1)
P(1)-C(16)	1.85 (1)	P(1)-C(22)	1.84 (1)
P(2)-C(11)	1.82 (2)	P(2)-C(28)	1.84 (1)
P(2)-C(34)	1.84 (1)	O(1)-C(1)	1.14 (2)
O(2)-C(2)	1.16 (1)	O(3)-C(3)	1.13 (2)
C(4)-C(5)	1.39 (2)	C(4)-C(10)	1.42 (2)
C(5)-C(6)	1.42 (2)	C(6)-C(7)	1.38 (2)
C(7)-C(8)	1.43 (3)	C(8)-C(9)	1.41 (2)
C(9)-C(10)	1.45 (2)	C(11)-C(12)	1.42 (2)
C(11)-C(15)	1.41 (2)	C(12)-C(13)	1.42 (3)
C(13)-C(14)	1.37 (2)	C(14)-C(15)	1.43 (2)
C(16)-C(17)	1.38 (2)	C(16)-C(21)	1.37 (2)
C(17)-C(18)	1.38 (2)	C(18)-C(19)	1.35 (2)
C(19)-C(20)	1.35 (2)	C(20)-C(21)	1.39 (2)
C(22)-C(23)	1.38 (2)	C(22)-C(27)	1.39 (2)
C(23)-C(24)	1.36 (2)	C(24)-C(25)	1.36 (3)
C(25)-C(26)	1.36 (2)	C(26)-C(27)	1.36 (2)
C(28)-C(29)	1.35 (3)	C(28)-C(33)	1.39 (3)
C(29)-C(30)	1.38 (2)	C(30)-C(31)	1.34 (3)
C(31)-C(32)	1.36 (4)	C(32)-C(33)	1.36 (2)
C(34)-C(35)	1.41 (2)	C(34)-C(39)	1.36 (2)
C(35)-C(36)	1.36 (2)	C(36)-C(37)	1.37 (3)
C(37)-C(38)	1.39 (2)	C(38)-C(39)	1.38 (2)
Cent1[a]-Ti(1)	1.47	Cent2-Ti(1)	1.97

P(1)-Mn(1)-P(2)	101.7 (1)	P(1)-Mn(1)-C(1)	167.9 (4)
P(2)-Mn(1)-C(1)	89.0 (4)	P(1)-Mn(1)-C(2)	83.9 (5)
P(2)-Mn(1)-C(2)	159.1 (5)	C(1)-Mn(1)-C(2)	84.1 (6)
P(1)-Mn(1)-C(3)	93.7 (4)	P(2)-Mn(1)-C(3)	100.8 (3)
Mn(1)-P(1)-C(4)	121.4 (3)	Mn(1)-P(1)-C(16)	112.7 (4)
C(4)-P(1)-C(16)	104.1 (6)	Mn(1)-P(1)-C(22)	115.3 (5)
C(4)-P(1)-C(22)	98.7 (6)	C(16)-P(1)-C(22)	102.0 (5)
Mn(1)-P(2)-C(11)	120.1 (3)	Mn(1)-P(2)-C(28)	109.9 (4)
C(11)-P(2)-C(28)	101.0 (6)	Mn(1)-P(2)-C(34)	121.3 (5)
C(11)-P(2)-C(34)	101.0 (6)	C(28)-P(2)-C(34)	100.1 (6)
Mn(1)-C(1)-O(1)	171.9 (9)	Mn(1)-C(2)-O(2)	175 (1)
Mn(1)-C(3)-O(3)	176 (1)	P(1)-C(4)-C(5)	113 (1)
P(1)-C(4)-C(10)	118.9 (8)	C(5)-C(4)-C(10)	128 (1)
C(4)-C(5)-C(6)	129 (2)	C(5)-C(6)-C(7)	130 (1)
C(6)-C(7)-C(8)	128 (1)	C(7)-C(8)-C(9)	129 (2)
C(8)-C(9)-C(10)	128 (2)	C(4)-C(10)-C(9)	128 (1)
P(2)-C(11)-C(12)	127 (1)	P(2)-C(11)-C(15)	124.9 (9)
C(12)-C(11)-C(15)	108 (1)	C(11)-C(12)-C(13)	107 (1)
C(12)-C(13)-C(14)	110 (1)	C(13)-C(14)-C(15)	107 (2)
C(11)-C(15)-C(14)	108 (1)	P(1)-C(16)-C(17)	118.9 (9)
P(1)-C(16)-C(21)	122 (1)	C(17)-C(16)-C(21)	119 (1)
C(16)-C(17)-C(18)	121 (1)	C(17)-C(18)-C(19)	120 (2)
C(18)-C(19)-C(20)	120 (2)	C(19)-C(20)-C(21)	120 (1)
C(16)-C(21)-C(20)	120 (1)	P(1)-C(22)-C(23)	122 (1)
P(1)-C(22)-C(27)	122 (1)	C(23)-C(22)-C(27)	116 (1)
C(22)-C(23)-C(24)	122 (2)	C(23)-C(24)-C(25)	120 (2)
C(24)-C(25)-C(26)	120 (2)	C(25)-C(26)-C(27)	120 (2)
C(22)-C(27)-C(26)	122 (1)	P(2)-C(28)-C(29)	123 (1)
P(2)-C(28)-C(33)	120 (1)	C(29)-C(28)-C(33)	117 (1)
C(28)-C(29)-C(30)	121 (2)	C(29)-C(30)-C(31)	121 (2)
C(30)-C(31)-C(32)	119 (2)	C(31)-C(32)-C(33)	120 (2)
C(28)-C(33)-C(32)	122 (2)	P(2)-C(34)-C(35)	119 (1)
P(2)-C(34)-C(39)	122.1 (8)	C(35)-C(34)-C(39)	119 (1)
C(34)-C(35)-C(36)	120 (1)	C(35)-C(36)-C(37)	120 (1)
C(36)-C(37)-C(38)	121 (1)	C(37)-C(38)-C(39)	118 (2)
C(34)-C(39)-C(38)	122 (1)	Cent1-Ti(1)-Cent2	175.8

[a] Cent1 is the centroid of the C_7 ring, Cent2 is that of the C_5 ring.

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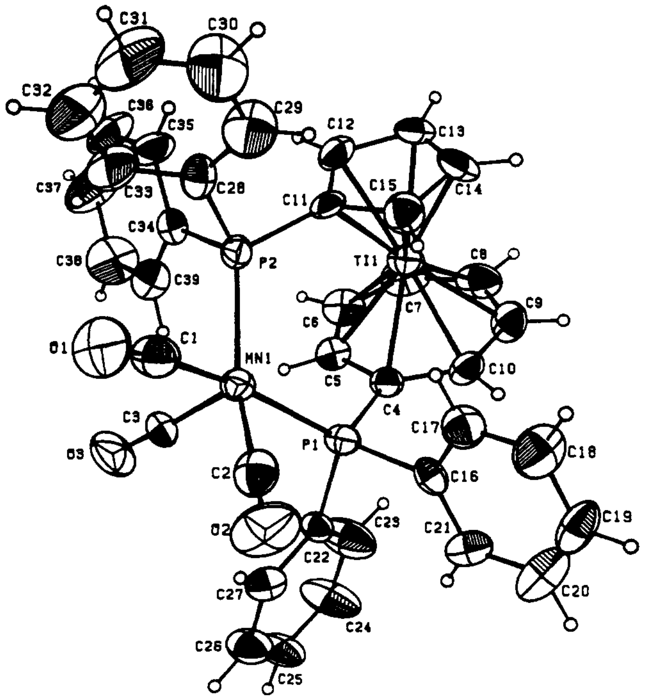

Figure 2. Molecular structure and atom-labeling scheme for 4.

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 4

color/shape	green/parallelepiped
fw	712.44
space group	$P\bar{1}$
temp, °C	20
cell constants[a]	
a, Å	10.135 (4)
b, Å	10.366 (4)
c, Å	18.484 (4)
α, deg	102.80 (3)
β, deg	93.60 (3)
γ, deg	116.42 (4)
cell vol, Å^3	1666.5
formula units/unit cell	2
D_{calc}, g cm^{-3}	1.42
μ_{calc}, cm^{-1}	7.82
diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ
λ(Mo Kα radiation, graphite monochromator), Å	0.710 73
max cryst dimens, mm	0.05 × 0.13 × 0.23
scan width	$0.80 + 0.35 \tan \theta$
std reflns	200, 020, 002
decay of stds	±2%
no. of reflns measd	5718
2θ range, deg	$2 \leq 2\theta \leq 25$
range of hkl	+13,±10,±23
no. of reflns obsd [$F_o \geq 5\sigma(F_o)$][b]	1981
computer program[c]	SHELX[10]
structure soln	SHELXS[11]
no. of params varied	415
weights	$[\sigma(F_o)^2 + 0.0007F_o^2]^{-1}$
GOF	0.49
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.061
R_w	0.069
largest feature final diff map, e Å^{-3}	0.3

[a] Least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections $\theta > 14°$. [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref 12.

Table III. Final Fractional Coordinates for $HMn(CO)_3[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]$ (4)

atom	x/a	y/b	z/c	B(eqv),[a] Å^2
Mn(1)	0.3256 (2)	0.6033 (2)	0.21574 (9)	2.11
Ti(1)	0.1950 (2)	0.1458 (2)	0.2634 (1)	2.56
P(1)	0.3718 (3)	0.5559 (3)	0.3307 (2)	2.00
P(2)	0.1740 (3)	0.3614 (3)	0.1374 (1)	2.12
O(1)	0.340 (1)	0.736 (1)	0.0894 (5)	5.63
O(2)	0.597 (1)	0.8933 (9)	0.2770 (5)	5.41
O(3)	0.0980 (9)	0.6929 (9)	0.2579 (5)	4.27
C(1)	0.328 (2)	0.675 (1)	0.1347 (7)	3.32
C(2)	0.489 (1)	0.779 (1)	0.2563 (7)	3.37
C(3)	0.186 (1)	0.657 (1)	0.2443 (7)	2.42
C(4)	0.275 (1)	0.365 (1)	0.3428 (6)	2.16
C(5)	0.120 (1)	0.299 (1)	0.3219 (6)	2.33
C(6)	0.010 (1)	0.151 (1)	0.3169 (7)	2.87
C(7)	0.027 (2)	0.034 (2)	0.3310 (7)	3.32
C(8)	0.162 (2)	0.030 (2)	0.3530 (7)	3.60
C(9)	0.311 (2)	0.148 (1)	0.3694 (7)	3.08
C(10)	0.361 (1)	0.299 (1)	0.3642 (6)	2.29
C(11)	0.202 (1)	0.206 (1)	0.1511 (6)	2.23
C(12)	0.091 (1)	0.054 (1)	0.1376 (6)	2.77
C(13)	0.167 (2)	−0.026 (2)	0.1532 (7)	3.25
C(14)	0.318 (2)	0.069 (2)	0.1755 (7)	3.77
C(15)	0.342 (2)	0.215 (2)	0.1736 (7)	3.16
C(16)	0.573 (1)	0.618 (1)	0.3628 (7)	2.49
C(17)	0.653 (2)	0.584 (1)	0.3115 (7)	3.11
C(18)	0.801 (2)	0.623 (2)	0.3339 (8)	4.24
C(19)	0.870 (2)	0.698 (2)	0.4064 (9)	3.33
C(20)	0.793 (2)	0.732 (2)	0.4579 (9)	4.07
C(21)	0.643 (2)	0.693 (1)	0.4362 (7)	2.87
C(22)	0.326 (1)	0.657 (1)	0.4123 (6)	2.12
C(23)	0.274 (2)	0.595 (2)	0.4700 (8)	4.96
C(24)	0.241 (2)	0.669 (2)	0.5300 (8)	5.15
C(25)	0.257 (2)	0.808 (2)	0.5345 (8)	4.12
C(26)	0.314 (2)	0.876 (2)	0.4803 (7)	3.85
C(27)	0.346 (1)	0.800 (1)	0.4195 (7)	3.00
C(28)	0.203 (1)	0.354 (1)	0.0398 (7)	2.64
C(29)	0.299 (2)	0.310 (2)	0.0094 (8)	5.09
C(30)	0.320 (2)	0.309 (2)	−0.064 (1)	6.78
C(31)	0.250 (2)	0.358 (2)	−0.1063 (9)	5.98
C(32)	0.156 (2)	0.408 (2)	−0.077 (1)	5.88
C(33)	0.133 (2)	0.405 (2)	−0.0051 (8)	4.40
C(34)	−0.032 (1)	0.277 (1)	0.1223 (7)	2.71
C(35)	−0.118 (2)	0.158 (2)	0.0567 (7)	3.76
C(36)	−0.270 (2)	0.093 (2)	0.0454 (8)	4.20
C(37)	−0.340 (2)	0.133 (2)	0.1002 (9)	5.04
C(38)	−0.259 (2)	0.247 (2)	0.1661 (9)	4.79
C(39)	−0.105 (1)	0.318 (1)	0.1744 (7)	2.98

[a] $B(\text{eqv}) = {}^4/_3[a^2\beta(11) + b^2\beta(22) + c^2\beta(33) + ab(\cos \gamma)\beta(12) + ac(\cos \beta)\beta(13) + bc(\cos \alpha)\beta(23)]$.

The three carbonyl groups, two phosphine ligands, and a hydrogen atom form a distorted octahedron around the manganese atom. The phosphine groups are cis with a P(1)–Mn(1)–P(2) angle of 101.7 (1)°. The phosphorus atoms, C(1), and C(2) distort from an octahedral geometry toward the hydrogen position (C(3) is trans to the H position). The P(1)–Mn(1)–C(1) and P(2)–Mn(1)–C(2) angles are 167.9 (4) and 159.1 (5)°, respectively, with average Mn–P and Mn–C distances of 2.34 (1) and 1.80 (1) Å. Although the hydride was not directly observed in difference Fourier maps, its position from the geometry of the other ligands on manganese is unequivocal.

The average Mn–P distance of 2.34 (1) Å is slightly longer than observed in *trans,mer*-$HMn(CO)_3(PMe_2Ph)_2$[6] (Mn–P = 2.255 (2) Å) or in *trans,mer*-$HMn(CO)_3(PPh_3)_2$[9] (Mn–P = 2.267 (2) Å). In the title compound 4 the phosphines are trans to carbonyl ligands and the lengthening is probably a trans effect. The Mn–CO separations in all three compounds average 1.80 Å. Each structure exhibits similar distortions of the ligands cis to the H position toward this site.

As we have previously observed for complexes 5 and 6,[1,2] the titanium sandwich structure is unaffected by bonding to the transition-metal carbonyl fragments. The average bonding parameters are as follows: Ti–C(η^5) = 2.30 (1) Å

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[9] Hayakawa, H.; Nakayama, H.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2041.

(4), 2.34 (3) Å (1), 2.31 (2) Å (5), 2.31 (1) Å (6); Ti–C(η^7) = 2.19 (2) Å (4), 2.19 (5) Å (1), 2.19 (1) Å (5), 2.19 (2) Å (6); Centroid(η^5)–Ti–Centroid(η^7) = 175.8° (4), 175.8° (1), 173.5° (5), 175.8° (6). In 4–6, the phosphorus atoms show similar deviations from their respective aromatic carbon fragment planes of ca. 0.2 Å toward Ti for the C_7 ring and 0.08 Å away from Ti for the C_5 ring.

Experimental Section

All operations were carried out under an argon atmosphere with Schlenk of glovebox techniques. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus pentoxide. Hexane, benzene, and toluene were distilled under argon from sodium–potassium alloy, while dichloromethane was distilled under argon from calcium hydride. $Mn_2(CO)_{10}$ was purchased from Strem Chemicals, whereas (η^5-$C_5H_4PPh_2$)(η^7-$C_7H_6PPh_2$)Ti (1) was prepared by a literature method.[1] NMR spectra were recorded on a Varian XL-200 or XL-300 spectrometer, respectively, while IR spectra were obtained on a Perkin-Elmer 1310 or Mattson Cygnus 100 FTIR spectrometer. Column chromatography was carried out under argon by using CAMAG neutral-grade alumina. The alumina was heated under vacuum on a rotary evaporator to remove oxygen and water and then deactivated with 5% (by weight) argon-saturated water and stored under argon until use.

$HMn(CO)_3[(\eta^5$-$C_5H_4PPh_2)(\eta^7$-$C_7H_6PPh_2)Ti]$ (4). A 100-mL Schlenk flask was charged under argon with (η^5-$C_5H_4PPh_2$)(η^7-$C_7H_6PPh_2$)Ti (0.82 g, 1.43 mmol), $Mn_2(CO)_{10}$ (0.28 g, 0.71 mmol), and 60 mL of toluene. The reaction mixture was heated at reflux with stirring for 40 h. After this period, the hot solution was filtered through a frit and the latter was washed with a small amount of toluene. The solvent was removed under vacuum, and the resulting residue was washed several times with hexane and redissolved in toluene. The solution was then evaporated onto a small amount of alumina, and the residue was added to a dry-packed alumina column. Elution with hexane/toluene (1:1) brought down a green band, which was collected under argon. The solvent was removed under reduced pressure to give 1.15 g (57%) of 4 as a green solid. An analytical sample was obtained by recrystallization from dichloromethane/hexane at −20 °C as blue-green crystals. Anal. Calcd for $C_{78}H_{60}Mn_2O_6Ti_2P_4$: C, 64.84; H, 4.25. Found: C, 66.00; H, 4.04. IR (toluene): 1997 (s), 1925 (s), 1907 (s), 1727 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −6.11 (dd, 1 H, Mn–H), 5.20–6.65 (m, 10 H, C_5H_4 and C_7H_6), 7.14–8.13 (m, 20 H, C_6H_5). ^{31}P NMR (toluene): δ 64.0 (d, C_5–P, J_{P-P} = 46.0 Hz), 89.4 (d, C_7–P, J_{P-P} = 46.0 Hz). MS: *m/e* 712 (4, M$^+$), 628 (28, M − 3CO)$^+$, 572 (100, M − $Mn(CO)_3H$)$^+$.

X-ray Data Collection, Structure Determination, and Refinement. A green single crystal of the title compound 4 was mounted in a thin-walled glass capillary under argon and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P\bar{1}$. Subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. All crystals attempted were weak, and only 1981 reflections were observed out of the 5718 measured reflections in the best crystal attempted. A summary of data collection parameters is given in Table II.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Least-squares refinement with isotropic thermal parameters led to R = 0.082. The hydrogen coordinated to the manganese atom could not be located and was not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.061 and R_w = 0.069. The final values of the positional parameters are given in Table III.

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Supplementary Material Available: Tables SI–SIII, listing fractional coordinates for H atoms, thermal parameters, and least-squares planes results (7 pages); Table SIV, listing observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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