in a tin-ferrocene amine complex. We are currently investigating the chemical shift-structure relationships in a number of different stannacarboranes to see if this is indeed the case.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-9100048), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. Anil Saxena for his assistance during the synthesis of germanium adducts. The help and assistance of Professor T. P. Fehlner of the University of Notre Dame and Dr. R. L. Cerny and Mr. C. Jacoby of the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8211164), is also gratefully acknowledged.

Supplementary Material Available: Mass spectrometric data (Table S-1) for IV–VI and X–XII, a summary of crystallographic data for IV, X(A), and X(B) (Table S-2), atomic coordinates for X(B) (Table S-3), bond lengths and angles for IV, X(A), and X(B) (Table S-4), anisotropic displacement coefficients for IV, X(A), and X(B) (Table S-5), H atom coordinates and isotropic displacement coefficients for IV and X(A) (Table S-6), a perspective view of X(B) (Figure S-2B) showing the atom numbering scheme, and compositions of the molecular orbitals in compounds XIII (Table S-10), XIV (Table S-11), and XV (Table S-12) (61 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of the Isomers of (1-Phosphino-η^3-pentenyl)tricarbonylmanganese

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Diphenylphosphine reacts with η^5-pentadienyltricarbonylmanganese (1) to give isomers Mn[P(Ph)$_2$CH$_2$-η^3-CHCHCHCH$_3$](CO)$_3$ (2) and Mn[P(Ph)$_2$CH$_2$CH$_2$-η^3-CHCHCH$_2$](CO)$_3$ (3). In both cases, phosphorus is added stereoselectively to the terminal carbon atom. Single-crystal X-ray diffraction studies of 2 and 3 confirm the unprecedented formation of the novel [1-(diphenylphosphino)-η^3-pentenyl]tricarbonylmanganese complexes in which the phosphahexenyl ligand is bonded to the manganese center through an η^3 interaction and also by phosphorus coordination affording six- and seven-membered "pseudo"-ring structures. Crystals of 2 are orthorhombic, space group $Pna2_1$ with a = 8.844 (1) Å, b = 16.806 (2) Å, c = 12.629 (1) Å, and Z = 4. The structure was refined to discrepancy indices of R = 0.0596 and R_w = 0.0602 for 1468 reflections having $I > 3\sigma(I)$. Crystals of 3 are monoclinic, space group $P2_1/a$, with a = 10.630 (7) Å, b = 11.979 (8) Å, c = 14.27 (1) Å, β = 92.32 (6)°, and Z = 4. The structure was refined to discrepancy indices of R = 0.0641 and R_w = 0.0712 for 1735 reflections having $I > 3\sigma(I)$. The two complexes have distorted-octahedral geometries with important differences both in lengths within the phosphino-η^3-pentenyl systems and for the bonding parameters of the manganese ions. The metal carbonyl distances also show significant differences from one complex to the other. Monitoring of the reaction by IR and NMR (^{31}P, ^{1}H) spectroscopy showed that the addition of PHPh$_2$ to 1 proceeds by initial conversion to 2 and subsequent formation of 3, with no evidence for preliminary interaction at either the manganese center or one of the CO carbon atoms. The reactions of *cis*-MnBr(CO)$_4$PHPh$_2$ (7a) and *fac*-MnBr(CO)$_3$(PHPh$_2$)$_2$ (8a) with C$_5$H$_7$SnBu$_3$ to initially afford compound 2, are also discussed. The crystal of 7a is monoclinic, space group $P2_1/c$ with a = 11.325 (5) Å, b = 10.342 (3) Å, c = 14.813 (5) Å, β = 95.08 (3)°, and Z = 4. The structure was refined to values of R = 0.0495 and R_w = 0.0540 for 2001 reflections with $I > 3\sigma(I)$. The complex has a pseudooctahedral geometry with the bromine and diphenylphosphine ligands cis to each other.

Introduction

We recently described[1] studies on the reactivity of C$_5$H$_7$Mn(CO)$_3$ with secondary amines, the results of which support the occurrence of a 1,5-addition of the –NH function to the pentadienyl ligand, followed by coordination of the nitrogen atom to the manganese center and ultimately affording (1-amino-1–3-η^3-pentenyl)tricarbonylmanganese complexes. In order to clarify the key factors that determine the reactivity patterns in C$_5$H$_7$-Mn(CO)$_3$, we turned to the study of diphenylphosphine to explore how the PH function would act on the pentadienyl fragment. In this regard, the reactivity of complexes such as LM(CO)$_n$ [n = 3: M = Mn, L = Cp;[2] M = Mn, L = cycloheptadienyl;[3,4] M = Mn, Fe$^+$, L = cyclohexadienyl,[4] pentadienyl,[5] oxopentadienyl.[6] n = 4: M = Mn, L =

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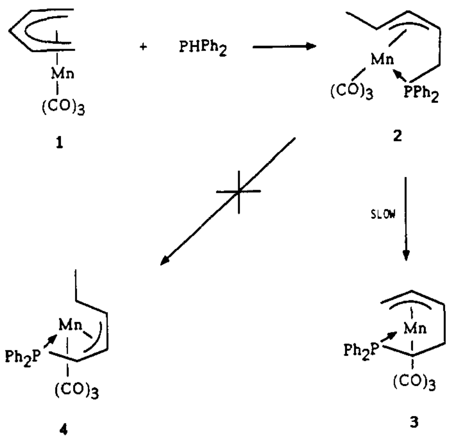
Scheme I



allyl[7]] with tertiary phosphines has been widely studied. Contrastingly, the number of reactions with secondary phosphines seems remarkably small for metal–carbonyl compounds,[8] and to our knowledge there are no examples involving species such as $LM(CO)_n$ (L = dienyl).

While related intramolecular organometallic-coordination compounds have been isolated as main reaction products from the reactions of metal complexes with benzylphosphine or tolylphosphine, few have been isolated as acyclic compounds from unsaturated derivatives.[9] As part of a program to study the reactivity of $C_5H_7Mn(CO)_3$ toward neutral nucleophiles, we describe in this paper the synthesis and structure of a new class of [1-(diphenylphosphino)-2–4(or 3–5)-η^3-pentenyl]tricarbonylmanganese complexes, which allow for useful comparisons with the secondary amine derivatives.

Synthetic Results and Discussion

The synthesis of compounds $Mn[P(Ph)_2CH_2\text{-}\eta^3\text{-}CHCHCHCH_3](CO)_3$ (**2**) and $Mn[P(Ph)_2CH_2CH_2\text{-}\eta^3\text{-}CHCHCH_2](CO)_3$ (**3**) is summarized in Scheme I. Isomers **2** and **3** were generally prepared in an approximate 4:1 ratio, at room temperature, from the reaction of $C_5H_7Mn(CO)_3$ (**1**) with 1 equiv of $PHPh_2$, in a combined yield of 41%. Several recrystallizations from diethyl ether/hexane at 0 °C gave **2** as lemon yellow and **3** as pale yellow crystals, **2** being more soluble in hexane than **3**. Both complexes are readily soluble in most organic solvents and slightly air sensitive in solution. Spectroscopic characterization proved that the phosphorus atom had added stereoselectively to the terminal carbon atom on the pentadienyl ligand and had also become coordinated to the manganese ion, similar to the situation found in the related neutral aminopentenyl derivatives[1] $Mn\leftarrow N(R_2)(\eta^3\text{-}CHCHCHCH_2CH_3)(CO)_3$ [$R_2 = (CH_2)_n$ (n = 4, 5), $O(CH_2)_4$, $HN(CH_2)_4$, $R = C_2H_5$ or $R = CH_3$, C_6H_{11}].

When a stoichiometric ratio of reactants was used, infrared spectroscopic monitoring revealed that the reaction was complete after 5 h. However, heating of the mixture led to loss of the pentenyl ligand from isomers **2** and **3**. This feature contrasts with the reaction of **1** with amines, which required a ligand excess and refluxing conditions. It is important to note that pure **2** or **3** can be heated without decomposition (vide infra) for longer times than the reaction mixture. These differences could be attributed to the presence of a yellow solid (^{31}P δ = 59 ppm) in the reaction mixture which is simultaneously formed and seems to compete for $PHPh_2$ (see Experimental Section). This compound does not contain hydrocarbon ligands, as observed by ^1H NMR spectroscopy.

In contrast to the situation for tertiary phosphines,[5a] spectroscopic monitoring of the above reaction failed to reveal any η^3-pentadienyl intermediates such as $Mn(\eta^3\text{-}C_5H_7)(CO)_3(PHPh_2)$ (**5**). An attempt to prepare such an intermediate by the addition of diphenylphosphine to $Mn(\eta^3\text{-}C_5H_7)(CO)_4$[10] (**6**) at room temperature did not succeed, as only starting materials were observed. However, when the mixture was refluxed for 4 h in cyclohexane, the ν(CO) patterns of **2** and **3** were clearly observed along with the corresponding bands for $Mn_2(CO)_{10}$. Again, no IR evidence of complex **5** has been observed, suggesting that this reaction involves the well-known $\eta^3 \rightarrow \eta^5$ pentadienyl conversion between **6** and **1**, which occurs after 80 min in refluxing n-hexane.[11] The absence of the corresponding ν(CO) bands for complex **1** (2025, 1957, 1937 cm^{-1}, hexane) in the IR spectrum may be attributed to the fact that immediately after being formed, it rapidly reacts with the $PHPh_2$ present in the reaction mixture, as would be expected on the basis of the mild conditions required for the reaction between **1** and $PHPh_2$. As a result of the refluxing conditions used in this reaction, the yields of isomers **2** and **3** are very poor, thereby preventing their isolation.

^1H and ^{31}P NMR experiments confirm that the initial reaction involves the apparent nucleophilic addition of the phosphine to the pentadienyl ligand (see Scheme I), with formation of the neutral (diphenylphosphino)-2–4-η^3-pentenyl derivative **2** almost immediately after the $PHPh_2$ addition, while complex **3** is observed a few minutes later. The reaction mixture showed a 4:1 ratio for **2** and **3** after 5 h at room temperature. Thus, it was of interest to determine whether the reaction of **1** and $PHPh_2$ proceeds exclusively via an 1,5-addition to give complex **2**, which after isomerization could afford complex **3**, or if both complexes **2** and **3** are formed independently in the reaction mixture, in which case 1,2- and 1,5-additions would be implicated. Pure complexes **2** and **3** were heated under reflux in benzene for 21 and 70 h. In the case of **2** this leads to a slow isomerization to afford complex **3** in 10% and 17% yields, respectively. Addition of 0.5 equiv of $PHPh_2$ to a benzene solution of **2** under the same conditions gave identical results, while for **3**, heating in refluxing benzene for 70 h does not show interconversion. Thus, there is convincing evidence showing that the isomerization occurred from **2** to **3**, but the high energy involved in the isomerization process may suggest that, in principle, the 1,2-addition cannot be entirely discounted, although it is not the preferred route.

On the basis of these observations and without evidence for the formation of any transient intermediates in these reactions, we suspect that a possible mechanism may involve a classical diene hydride intermediate such as $[Ph_2PCH_2{=}CH{=}CHCH{=}CH_2Mn(H)(CO)_3]$. Subsequent hydride attack on a terminal carbon (1,5-addition) or an internal carbon (1,2-addition) of the diene might induce formation of complexes **2** and **3**, respectively.

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The syn stereoselectivity leading to 2, which does not retain the cisoid geometry of the original pentadienyl ligand, is reasonable given the facile anti–syn isomerization known for methylallylmanganese[12] and methylpentadienyl complexes[1,13] and will be further favored by the presence of the PPh_2 group which provides large interactions with the other internal (anti) substituent. It is thus reasonable to implicate a π–σ–π mechanism, in which a diene hydride intermediate gives a σ-allyl intermediate, probably a 16-electron system, in which the Mn←P bond, is retained, consistent with our mass spectral results (vide infra). Considering the 1,5-addition, a C–C rotation of the σ-allyl species would afford the methyl group in the syn position. The rotation would be accompanied by ligand rearrangements for the five-coordinate intermediate giving the π-complex 2. A second alternative is to consider the 1,2-addition, from which the π diene hydride intermediate affords a similar σ-allyl 16-electron system, which rearranges directly to complex 3. Conversion of 2 to 3 could take place by going back to the diene hydride intermediate.

There is no evidence for the presence of the third possible isomer 4. However, nitrogen analogs of isomer 4 have been exclusively isolated when the more electronegative and smaller-NH function was used.[1] In accord with these and previously discussed results, it is clear that the secondary diphenylphosphine, as well as secondary amines, undergo addition to the η^5-pentadienyl ligand in complex 1. Recently, evidence has been obtained of an amino-2–4-η^3-pentenyl analog of complex 2, arising from the reaction of cyclohexylamine with 1.[14]

Complexes 2 and 3 cannot be distinguished in the IR spectra since they show the same three strong ν(CO) absorption bands at 2000, 1921, and 1912 cm^{-1} in hexane. However, by comparison of the ν(CO) values of 1 with those of 2 and 3, one can clearly observe that there is much greater electron density at the metal center, as a result of the P→Mn bonds in the last two compounds. The intensity patterns are consistent with a *fac* arrangement for the three carbonyl groups,[5a,7] as was also confirmed by X-ray diffraction studies (vide infra). Very similar ν(CO) patterns and frequencies are observed for complexes with detached phosphines, such as $Mn(\eta^3\text{-}C_5H_7)(CO)_3(PMe_2Ph)$ (2000, 1935, 1903 cm^{-1}, Nujol)[5a] or $Mn(\eta^3\text{-}C_3H_5)(CO)_3\text{-}(PMe_2Ph)$ (2000, 1930, 1908 cm^{-1}, pentane).[7] Not surprisingly, the presence of an amino fragment in the pentenyl ligand of $Mn(\eta^3\text{-}CH(N(CH_2)_5CHCHCH_2CH_3)\text{-}(CO)_3PMe_2Ph$ leads to even greater frequency shifts to 1977, 1901, and 1881 cm^{-1} (hexane),[1] thus reflecting the smaller π-acceptor ability of this aminopentenyl fragment as compared to the phosphino-η^3-pentenyl analogs.

The mass spectra of complexes 2 and 3 show base peaks corresponding to the $[Mn - C_5H_8PPh_2]^+$ fragment. This pattern differs from that found in the aminopentenyl complexes, in which the $[Mn - C_5H_8NR_2]^+$ fragment was never observed.[1] Also, for terminal tertiary phosphines in $[Mn(\eta^3\text{-}C_5H_7)(CO)_3L]$ complexes, the corresponding fragment $[C_5H_7MnPR_3]^+$ always appears in low intensity (L = PMe_3, 23%; L = PMe_2Ph, 33%; L = PBu_3, 16%).[5a] The $[MnPPh_2]^+$ fragments are present at 45 and 34% in 2 and 3, respectively. These facts suggest greater stability for the P→Mn bonds in the phosphino-η^3-pentenyl chelate systems, as compared to the N→Mn and R_3P→Mn bonds.

Double-resonance techniques allowed the complete NMR spectral assignments for complex 2, showing diastereomeric signals for the two H4 at 2.75 and 3.30 ppm in $CDCl_3$ or 2.05 and 2.50 ppm in C_6D_6. ^1H NMR spectra reveal that the phosphahexenyl fragment adopts a syn–anti conformation, as indicated by the trans and cis coupling pattern J_{12} = 10.6 and J_{23} = 7 Hz, respectively. The corresponding assignments for complex 3 were also confirmed by double-resonance experiments. Irradiation of the H1 resonance at 1.4 ppm led to the collapse of the doublet of triplets at 4.82 ppm to a triplet (J = 7.5 Hz). The same coupling constant (7.5 Hz) is also observed when the quartet at 4.15 ppm due to H3 collapses to a triplet upon irradiation of H4 at 2.08 ppm, indicating that H2 and H3 are cis and therefore that an anti conformation has been adopted by the phosphahexenyl ligand in solution, as is also observed in the solid state (vide infra). The torsion angles for C2–C3–C4–H4A and C2–C3–C4–H4B are −4.6 (0.8) and −123.6 (0.7)°, respectively, which suggests that H4A is almost coplanar with the allyl fragment. This fact is also reflected in solution, where a small allylic coupling is observed for the signal at 2.79 ppm, which upon irradiation of H2 at 4.82 ppm is simplified to a triplet. The $^{13}C\{^1H\}$ NMR spectra confirm the lack of symmetry in the pentenyl fragment for both isomers (see Experimental Section). Notably, couplings from the phosphorus nucleus were observed for carbon atoms C4, C3, and C2 in complex 2 and C5 and C4 in complex 3. It has been observed that C1 also shows a 4-Hz coupling when the spectrum of 3 is measured at 22.49 MHz. A substantial high-field shift for C3 (δ 46.3 ppm, J_{CH} = 163 Hz) in complex 2 was observed, probably reflecting an important steric effect on this "pseudocyclic" complex. Such signals for common substituted "allyl" systems have typical δ values of ~70 ppm[15] (carbon atom C3 in complex 3, δ 74.8 ppm).

The ^{31}P NMR spectra show a very wide $\Delta\delta$ = 101 ppm between the isomers, i.e., complex 2 having δ = −25 ppm and complex 3 having δ = 76 ppm, giving evidence of the different structural requirements on both *pseudo*ring structures. Correlations between ^{31}P chemical shifts and steric parameters of phosphametallacycloalkanes have been reported[16a] and demonstrate that torsional angles play a dominant role. Thus the heterocycles $(OC)_4MnPPh_2\text{-}(CH_2)_n$ (n = 4 and 5) show a $\Delta\delta$ = 46.5 ppm[16b] which is around half of the value found for the alicyclic structures reported here. The $\Delta\delta$ = 101 ppm value between 2 and 3 is therefore quite reasonable, given the steric congestion in complex 2, as revealed by the single-crystal X-ray diffraction studies (vide infra).

The related additions undergone by diphenylphosphine and secondary amines to the η^5-pentadienyl ligand motivated us to extend this study to the reaction between $MnBr(CO)_4PHPh_2$ (**7a**) or $MnBr(CO)_3(PHPh_2)_2$ (**8a**) and $C_5H_7SnBu_3$, to observe the reversal in the order of coordination of the phosphine and pentadienyl ligands. Both reactions led to the formation of isomer 2 in very low yields and traces of isomer 3. Reaction of *cis*-$MnBr(CO)_4PHPh_2$ (**7a**) with $C_5H_7SnBu_3$ after 4.5 h in refluxing THF afforded, after chromatography on alumina, complex 2 (6.6%), complex 1 (6.7%), complexes **8a** and **9a** (vide infra), and recovered starting materials $C_5H_7SnBu_3$ and complex **7a**.

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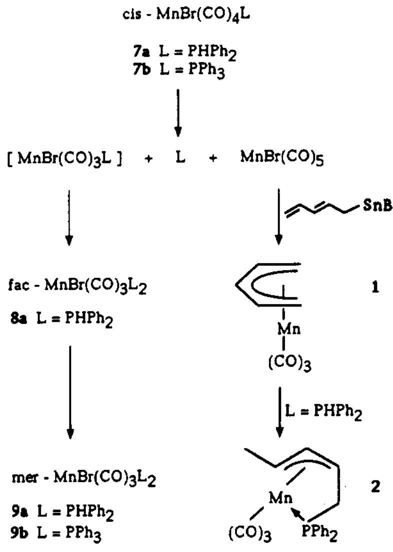
Scheme II



An even lower yield of complex **2** was isolated from the corresponding reaction with *fac*-$MnBr(CO)_3(PHPh_2)_2$ (**8a**). From these results, it was of interest to study the reaction mechanism for complexes **7a** and **8a** by ^{31}P NMR and IR spectroscopy. After an equimolar mixture of $C_5H_7SnBu_3$ and *cis*-$MnBr(CO)_4PHPh_2$ (**7a**) was heated in an NMR tube at 60 °C for 40 min, the spectrum revealed the presence of **8a** (^{31}P $\delta = 39$) and complex **7a** (^{31}P $\delta = 32$). After 3 h there was also evidence of *mer*-$MnBr(CO)_3(PHPh_2)_2$ (**9a**) (^{31}P $\delta = 47$), which arose by isomerization of the facial isomer **8a**. Finally, after 5.5 h at 60 °C the signal for complex **2** (^{31}P $\delta = -25$) was observed. These results, along with extensive studies[17-20] on the substitution reactions of halogenomanganese carbonyl compounds, support the pathway described in Scheme II. It has been found that heating a solution of pure *cis*-$MnBr(CO)_4PPh_3$ (**7b**) in chloroform leads directly to the meridional complex $MnBr(CO)_3(PPh_3)_2$ (**9b**) and $MnBr(CO)_5$.[18] The mechanism of this ligand-transfer reaction is unknown, but it has been proposed that dissociation of a phosphine group and formation of a carbonyl-bridged dimer are involved.[18] The postulated five-coordinate intermediate $[MnBr(CO)_3L]$ is the same as that assumed by Basolo and co-workers[21] for similar species in solution,[18,20] and similar processes may occur when diphenylphosphine is used. However, some differences are readily apparent. While complex *cis*-**7b** is obtained after 10 h of reflux in CH_2Cl_2, the corresponding complex **7a** could be isolated after 3 h at room temperature. All attempts to detect the facial isomer for L = PPh_3 **8b** failed, whereas complex **7a** easily forms an equilibrium mixture with the facial isomer **8a**. This *fac* isomer **8a** is the intermediate in the formation of the meridional isomer **9a**, and it has been proposed that steric interactions prevent the formation of the facial isomer for L = PPh_3.[18] The relief of steric strain for the *fac* complex with the smaller $PHPh_2$ is a reasonable explanation for its isolation and stability.

In Scheme II one observes that the formed $MnBr(CO)_5$ in the presence of $C_5H_7SnBu_3$ leads to complex **1**, which then reacts with the dissociated diphenylphosphine, affording complex **2** as already described. The low yield of **2** from this reaction is clearly reasonable given that complexes **8a** and **9a**, should have stronger Mn–P bonds. Also, heating of the reaction mixture led to disruption of the pentenyl–manganese bond in compound **2**.

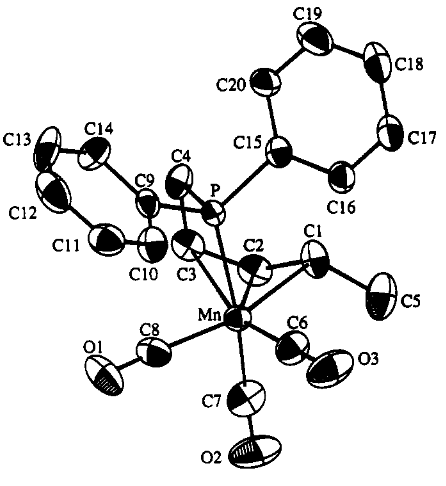


Figure 1. ORTEP diagram of [1-(diphenylphosphino)-η^3-2,4-pentenyl]tricarbonylmanganese (**2**).

The reaction of *fac*-$MnBr(CO)_3(PHPh_2)_2$ (**8a**) (^{31}P $\delta = 39$) with $C_5H_7SnBu_3$ in refluxing THF/C_6D_6 showed the formation of the *mer* complex **9a** (^{31}P $\delta = 47$) after several minutes. Further heating (14 h) of this mixture led to two new signals at δ −28 and 55 ppm which are attributable to complex **2** and, presumably, to the *mer–cis*-dicarbonyl species $MnBr(CO)_2(PHPh_2)_3$, respectively, according to the IR carbonyl bands (~1960 (s, br) and 1870 (s), $CHCl_3$) which are similar to those observed for $MnBr(CO)_2L_3$ complexes [L = $P(OEt)_3$ 1973 (s), 1888 (s); L = $P(OMe)_2Ph$ 1977 (s), 1885 (s); L = PMe_2Ph 1929 (s), 1851 (s)].[17] The NMR spectra further show a conversion to the *mer–cis*-dicarbonyl species (^{31}P $\delta = 55$) from the respective *mer* complex **9a** through the disappearance of the signal at 47 ppm. The final ^{31}P NMR spectrum after 17 h of reflux shows signals at 55, 47, 38, and −28 ppm in a relative ratio of 2:0.3:1.2:0.16, for the *mer–cis*-dicarbonyl, **9a**, **8a**, and **2** species, respectively. These results suggest the occurrence of isomerizations analogous to those previously reported for complexes of tertiary phosphines and phosphites, among other ligands.[17] However, the inertness of these isomers toward $C_5H_7SnBu_3$ is demonstrated by the extremely poor yield of complex **2** as compared to that obtained from the reaction with the tetracarbonyl complex **7a**, in which $MnBr(CO)_5$ is present. No evidence of interactions between the manganese–phosphine complexes and (pentadienyl)tributyltin was detected by ^{31}P NMR spectroscopy.

Structural Results and Discussion

Single crystals of **2** and **3** were obtained from diethyl ether–hexane solutions. Molecular structures are shown in Figures 1 and 2, and fractional atomic coordinates for all non-hydrogen atoms are given in Tables I and II, while bond lengths and bond angles are given in Tables III and IV. In both **2** and **3** the diphenylphosphine group is bonded to the pentadienyl group, leading to 1-phosphino-η^3-pentenyl fragments coordinated through the phosphorus atom and the allyl moiety to the manganese ion. The coordination spheres of the manganese atoms are completed with three carbonyl groups. The main difference between the isomers is that while in **2** the pentenyl group is bonded to the metal atoms through the three

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Table I. Positional Parameters ($\times 10^4$) with Their Estimated Standard Deviations and Temperature Factors ($Å^2 \times 10^3$) for $Mn[P(Ph)_2CH_2$-η^3-$CHCHCHCH_3](CO)_3$ (2)

atom	*x*	*y*	*z*	*U*
Mn	1168 (2)	4755 (1)	090	275 (2)
P	3590 (2)	4798 (1)	1462 (2)	262 (4)
O1	110 (1)	6497 (4)	495 (8)	67 (2)
O2	−1852 (9)	4707 (7)	−216 (8)	75 (3)
O3	−36 (1)	4633 (6)	2854 (7)	72 (3)
C1	164 (1)	3456 (5)	643 (7)	36 (2)
C2	180 (1)	3846 (6)	−312 (8)	37 (2)
C3	286 (1)	4485 (6)	−498 (7)	34 (2)
C4	430 (1)	4549 (6)	120 (7)	34 (2)
C5	37 (1)	2864 (6)	79 (1)	59 (3)
C6	27 (1)	4688 (7)	2053 (8)	42 (2)
C7	−65 (1)	4723 (7)	166 (8)	46 (2)
C8	116 (1)	5831 (6)	618 (9)	42 (2)
C9	441 (1)	5727 (5)	1857 (7)	28 (2)
C10	366 (1)	6168 (6)	2641 (9)	39 (2)
C11	422 (1)	6864 (7)	304 (1)	46 (2)
C12	557 (2)	7142 (6)	265 (1)	57 (3)
C13	637 (1)	6733 (7)	192 (1)	58 (3)
C14	583 (1)	6025 (6)	1530 (9)	41 (2)
C15	440 (1)	4099 (5)	2399 (7)	30 (2)
C(16)	346 (1)	3729 (6)	3133 (8)	35 (2)
C17	406 (1)	3224 (6)	3888 (9)	43 (2)
C18	560 (1)	3079 (6)	393 (1)	50 (3)
C19	650 (1)	3451 (7)	321 (1)	52 (3)
C20	593 (1)	3957 (6)	2441 (9)	38 (2)

Table II. Positional Parameters ($\times 10^4$) with Their Estimated Standard Deviations and Temperature Factors ($Å^2 \times 10^3$) for $Mn[P(Ph)_2CH_2CH_2$-η^3-$CHCHCH_2](CO)_3$ (3)

atom	*x*	*y*	*z*	*U*
Mn	5827 (1)	1215 (1)	2851 (1)	44 (1)
P	5276 (1)	−491 (1)	2208 (1)	42 (1)
C1	7103 (6)	366 (6)	3889 (6)	62 (3)
C2	7759 (6)	978 (6)	3248 (6)	67 (3)
C3	7671 (7)	753 (6)	2309 (7)	75 (3)
C4	7705 (7)	−406 (6)	1911 (6)	74 (3)
C5	6523 (6)	−727 (5)	1410 (5)	59 (2)
C6	4567 (7)	1160 (5)	3645 (5)	47 (2)
O6	3801 (5)	1132 (4)	4187 (4)	76 (2)
C7	6083 (7)	2639 (5)	3225 (5)	56 (2)
O7	6140 (6)	3567 (4)	3425 (5)	83 (2)
C8	5164 (7)	1804 (5)	1794 (5)	54 (2)
O8	4776 (5)	2251 (4)	1120 (4)	79 (2)
C9	3814 (6)	−618 (5)	1496 (4)	46 (2)
C10	2817 (6)	108 (6)	1618 (5)	64 (3)
C11	1697 (7)	−30 (8)	1098 (6)	79 (3)
C12	1578 (8)	−876 (8)	456 (6)	77 (3)
C13	2553 (8)	−1592 (7)	309 (5)	66 (3)
C14	3672 (7)	−1464 (5)	837 (5)	56 (2)
C15	5171 (6)	−1745 (5)	2933 (4)	48 (2)
C16	4261 (7)	−1751 (6)	3590 (5)	60 (2)
C17	4112 (9)	−2678 (7)	4171 (6)	80 (3)
C18	4878 (10)	−3593 (7)	4060 (7)	86 (4)
C19	5794 (9)	−3588 (7)	3413 (8)	93 (4)
C20	5944 (7)	−2661 (6)	2856 (6)	71 (3)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations for $Mn[P(Ph)_2CH_2$-η^3-$CHCHCHCH_3](CO)_3$ (2)

Bond Distances			
Mn–P	2.260 (2)	Mn–Cl	2.245 (8)
Mn–C2	2.230 (8)	Mn–C3	2.356 (8)
Mn–C6	1.667 (9)	Mn–C7	1.85 (1)
Mn–C8	1.841 (9)	P–C4	1.855 (9)
P–C9	1.791 (8)	P–C15	1.816 (9)
O1–C8	1.13 (1)	O2–C7	1.17 (1)
O3–C6	1.16 (1)	C1–C2	1.38 (1)
C1–C5	1.51 (1)	C2–C3	1.45 (1)
C3–C4	1.49 (1)		
Bond Angles			
P–Mn–C1	84.3 (2)	P–Mn–C2	90.0 (3)
P–Mn–C3	68.8 (2)	P–Mn–C6	100.0 (4)
P–Mn–C7	168.7 (3)	P–Mn–C8	91.7 (3)
C1–Mn–C2	36.0 (3)	C1–Mn–C3	65.8 (3)
C1–Mn–C6	98.4 (4)	C1–Mn–C7	93.5 (4)
C1–Mn–C8	158.2 (3)	C2–Mn–C3	36.6 (3)
C2–Mn–C6	132.3 (4)	C2–Mn–C7	81.9 (4)
C2–Mn–C8	122.9 (4)	C3–Mn–C6	160.8 (4)
C3–Mn–C7	100.1 (4)	C3–Mn–C8	92.8 (3)
C6–Mn–C7	91.2 (5)	C6–Mn–C8	103.4 (5)
C7–Mn–C8	86.2 (5)	Mn–P–C4	91.3 (3)
Mn–P–C9	120.0 (3)	Mn–P–C15	124.1 (3)
C4–P–C9	108.3 (4)	C4–P–C15	108.4 (4)
C9–P–C15	102.9 (4)	Mn–C1–C2	71.5 (5)
Mn–C1–C5	119.1 (6)	C2–C1–C5	119.8 (8)
Mn–C2–C1	72.6 (5)	Mn–C2–C3	76.4 (5)
C1–C2–C3	124.3 (8)	Mn–C3–C4	97.8 (5)
Mn–C3–C2	67.0 (5)	C2–C3–C4	121.4 (8)
P–C4–C3	102.0 (6)	Mn–C6–O3	179 (1)
Mn–C7–O2	174.6 (9)	Mn–C8–O1	176 (1)

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations for $Mn[P(Ph)_2CH_2CH_2$-η^3-$CHCHCH_2](CO)_3$ (3)

Bond Distances			
Mn–P	2.307 (2)	Mn–C1	2.215 (7)
Mn–C2	2.128 (7)	Mn–C3	2.207 (8)
Mn–C6	1.790 (7)	Mn–C7	1.805 (7)
Mn–C8	1.785 (7)	P–C5	1.804 (7)
P–C9	1.828 (6)	P–C15	1.830 (6)
C1–C2	1.383 (11)	C2–C3	1.367 (13)
C3–C4	1.502 (11)	C4–C5	1.470 (10)
C6–O6	1.147 (9)	C7–O7	1.149 (8)
C8–O8	1.161 (9)		
Bond Angles			
P–Mn–C1	89.9 (2)	P–Mn–C2	102.4 (2)
C1–Mn–C2	37.1 (3)	P–Mn–C3	81.5 (2)
C1–Mn–C3	65.9 (3)	C2–Mn–C3	36.7 (3)
P–Mn–C6	92.0 (2)	C1–Mn–C6	90.8 (3)
C2–Mn–C6	124.5 (3)	C3–Mn–C6	155.6 (3)
P–Mn–C7	171.1 (2)	C1–Mn–C7	98.9 (3)
C2–Mn–C7	85.1 (3)	C3–Mn–C7	102.4 (3)
C6–Mn–C7	87.5 (3)	P–Mn–C8	85.9 (2)
C1–Mn–C8	163.2 (3)	C2–Mn–C8	128.4 (3)
C3–Mn–C8	97.4 (3)	C6–Mn–C8	105.6 (3)
C7–Mn–C8	85.7 (3)	Mn–P–C5	102.0 (2)
Mn–P–C9	119.4 (2)	C5–P–C9	105.4 (3)
Mn–P–C15	121.5 (2)	C5–P–C15	107.0 (3)
C9–P–C15	100.2 (3)	Mn–C1–C2	68.1 (4)
Mn–C2–C1	74.9 (4)	Mn–C2–C3	74.8 (5)
C1–C2–C3	121.8 (7)	Mn–C3–C2	68.5 (4)
Mn–C3–C4	113.6 (5)	C2–C3–C4	123.5 (8)
C3–C4–C5	113.1 (6)	P–C5–C4	106.7 (5)
Mn–C6–O6	176.8 (6)	Mn–C7–O7	173.8 (6)
Mn–C8–O8	175.5 (6)	P–C9–C10	121.0 (5)
P–C9–C14	120.3 (5)		

central carbon atoms with a methyl group at one end of the chain and the PPh_2 group at the other end, 3 possesses a terminal η^3-bound enyl system at the opposite end of the PPh_2 group. Both isomers exhibit structures distorted from octahedral geometry, probably due in part to the steric requirements of the bifunctional ligands.

There are some important differences in bond lengths between 2 and 3. While both compounds show the same asymmetry in Mn–C distances observed in other η^3-pentadienyl complexes,[5a] the Mn–C bonds are uniformly longer in 2, with values ranging from 2.230 (8) to 2.245 (8) Å, compared to 3, for which the distances vary between 2.128 (7) and 2.215 (7) Å. In fact, the distances in 2 are also longer than those reported for other allyl-Mn[7] and η^3-pentadienyl–Mn complexes.[5a] The allylic C–C bond lengths also show some important differences for the two isomers. Thus, in 2 one C–C bond (C2–C3) is clearly longer than the other, 1.45 (1) vs 1.38 (1) Å, whereas in 3 any difference is less than the statistical uncertainties (1.38 (11) vs 1.367 (13) Å). The difference in 2 is also accompanied by a difference in the Mn–C1,3 bond lengths, 2.245 (8) vs 2.356 (8) Å, which might also be attributed to a partial

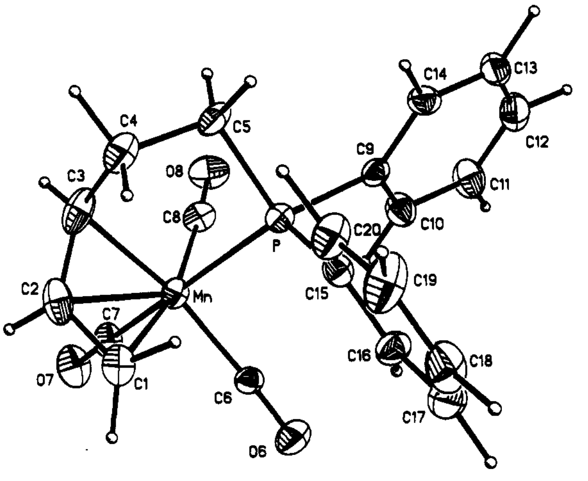

Figure 2. ORTEP diagram of [1-(diphenylphosphino)-η^3-3,5-pentenyl]tricarbonylmanganese (3).

Table V. Selected Torsion Angles (deg) for 2 and 3

Compound 2	
Mn-P-C4-C3	0.7 (4)
P-C4-C3-C2	-68.5 (7)
C4-C3-C2-C1	27.5 (6)
C1-Mn-P-C4	65.6 (4)
Compound 3	
Mn-P-C5-C4	43.2 (5)
C3-C4-C5-P	-53.4 (8)
C1-Mn-P-C5	-84.4 (3)
C1-C2-C3-C4	-43.9 (1.1)

contribution of a σ-allyl coordination mode and/or from the strain induced by coordination of the enyl-phosphine ligand. A weakening of the Mn-allyl coordination could also easily explain the significant shortening of the Mn-C6 bond.[22-24] The 1.45 (1) Å C-C distance is longer than those reported for the majority of allyl-manganese complexes.[25] The C-C-C angles of the η^3-pentadienyl fragment are all close to 120° and not different from others described in the literature.[26]

The Mn-P distances are 2.260 (2) and 2.307 (2) Å for **2** and **3**, respectively. The second value is similar to those found in some cyclic and acyclic manganese complexes. However, the value for **2** is unusual[25] but may also reflect the partial contribution of a σ-allyl bonding mode. Notably, it is accompanied by a longer trans Mn-CO distance, 1.85 (1) vs 1.805 (7) Å for **3**.

Some important torsion angles for complexes **2** and **3** are provided in Table V. While the torsion angle Mn-P-C4-C3 in **2** is 0.7 (4), Mn-P-C5-C4 in **3** is 43.2 (5). Similarly, P-C4-C3-C2 in **2** is -68.5 and C3-C4-C5-P in **3** is -53.4 (8). These values are an indication of the steric requirements of the two ring sizes, which are also manifested by the ^{31}P NMR spectra, for which significantly different shifts (-25 for **2** and 76.0 ppm for **3**) are found. This behavior has been previously observed in other phosphametallacycles.[16]

It is important to compare the structural features of **2** and **3** with those of aminopentenyl derivatives previously reported.[1] Unfortunately, detailed comparisons are not possible due to the large standard deviations in some of the parameters, but a trend to shorter Mn-C(η^3-pentenyl) distances can be observed in the amino derivatives. It can thus be seen that the Mn-C bond lengths in these η^3 systems tend to increase in the order aminopentenyl derivatives < **3** < **2**. The shorter distances in the first compounds are not so surprising in view of the smaller ring size present in these complexes. The trend in **2** and **3**, characterized by six- and seven-membered *pseudo*ring sizes, respectively, could also be ascribed to the steric requirements of the rings. A similar trend in Mn-C distance is observed in the phosphametallacycles of six and seven members[16b,c] although the observed variations are not as large as in **2** and **3**. It is also important to recognize that the Mn-N distances in the aminopentenyl complexes are practically equivalent to the sum of the covalent radii of the atoms, while the Mn-P distances in **2** and **3** are shorter than the corresponding sum and, as mentioned above, shorter in **2** than in **3**. In the phosphametallacycles previously mentioned, the Mn-P bond length does not suffer such large variations with ring size changes.

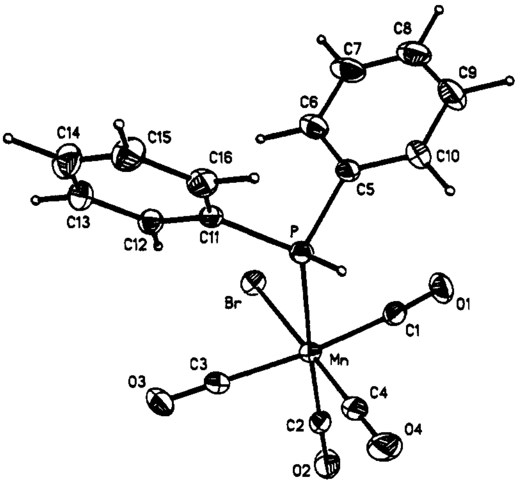

Figure 3. ORTEP diagram of cis-MnBr(CO)$_4$PHPh$_2$ (**7a**).

One of the most interesting results obtained from these studies is the fact that neither the phosphine nor the amine produces all three isomers that could be anticipated from the addition of the base to the pentadienyl group (see Scheme I). In the case of isomer **4**, only obtained with amines, the larger size of the phosphorus atom almost certainly could make the small pentanuclear ring rather unstable. Sterically, the formation of the corresponding aminopentenyl analogs of **2** and **3** would seem possible and, as pointed out earlier, there is now evidence of a primary amine derivative similar to **2**.[14] One could argue that, as has been previously discussed,[1] the nitrogen atom can delocalize its electron density into the organic unsaturated fragment for **4**, presumably producing a softer ligand which can coordinate more effectively to the relatively soft manganese(I) ion. In the case of the primary amine, isomer **2** could be stabilized. It can also be suggested that the softer PH group does not need this conjugation to stabilize the P→Mn bond.

Since no structural information on **7a** could be found, as very little exists on this type of complex, a single-crystal X-ray study was carried out for comparative purposes. The molecular structure of complex **7a** is shown in Figure 3. The fractional atomic coordinates for the non-hydrogen atoms are given in Table VI, while bond lengths and bond angles are found in Table VII. The structure consists of discrete molecules which show octahedral geometry with

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Table VI. Positional Parameters (×10^4) with Their Estimated Standard Deviations and Temperature Factors (Å^2 × 10^3) for $MnBr(CO)_4PHPh_2$ (7a)

atom	*x*	*y*	*z*	*U*
Br	3425 (1)	6561 (1)	7173 (1)	54 (1)
Mn	4533 (1)	7601 (1)	8545 (1)	42 (1)
P	2874 (1)	7437 (1)	9373 (1)	42 (1)
C1	3898 (4)	9192 (5)	8107 (3)	51 (2)
O1	3481 (4)	10103 (4)	7822 (3)	75 (1)
C2	5808 (4)	7803 (5)	7880 (4)	55 (2)
O2	6619 (4)	7952 (4)	7478 (4)	85 (2)
C3	5021 (4)	5914 (5)	8863 (3)	47 (2)
O3	5320 (3)	4894 (4)	9024 (2)	67 (1)
C4	5352 (4)	8336 (5)	9520 (4)	59 (2)
O4	5890 (4)	8810 (5)	10109 (4)	96 (2)
C5	1540 (4)	8287 (4)	8904 (3)	48 (2)
C6	779 (5)	7714 (6)	8255 (4)	63 (2)
C7	−236 (5)	8364 (7)	7876 (5)	85 (3)
C8	−476 (5)	9556 (7)	8158 (6)	97 (3)
C9	281 (7)	10160 (7)	8817 (7)	108 (4)
C10	1298 (5)	9517 (6)	9187 (5)	80 (2)
C11	2314 (4)	5881 (4)	9724 (3)	43 (1)
C12	2396 (4)	4794 (5)	9201 (3)	51 (2)
C13	1987 (5)	3613 (5)	9487 (4)	61 (2)
C14	1489 (6)	3528 (6)	10318 (5)	77 (2)
C15	1415 (5)	4610 (7)	10833 (4)	75 (2)
C16	1824 (4)	5787 (6)	10547 (4)	61 (2)

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations for $MnBr(CO)_4PHPh_2$ (7a)

	Bond Distances		
Br–Mn	2.532 (1)	Mn–P	2.339 (1)
Mn–C1	1.888 (5)	Mn–C2	1.831 (6)
Mn–C3	1.877 (5)	Mn–C4	1.814 (6)
P–C5	1.831 (5)	P–C11	1.821 (5)
C1–O1	1.119 (6)	C2–O2	1.148 (7)
C3–O3	1.127 (6)	C4–O4	1.131 (7)
	Bond Angles		
Br–Mn–P	91.5	Br–Mn–C1	87.0 (1)
P–Mn–C1	86.8 (2)	Br–Mn–C2	88.6 (2)
P–Mn–C2	177.4 (2)	C1–Mn–C2	90.6 (2)
Br–Mn–C3	85.5 (1)	P–Mn–C3	91.9 (1)
C1–Mn–C3	172.3 (2)	C2–Mn–C3	90.7 (2)
Br–Mn–C4	178.9 (2)	P–Mn–C4	89.5 (2)
C1–Mn–C4	93.5 (2)	C2–Mn–C4	90.5 (2)
C3–Mn–C4	94.0 (2)	Mn–P–C5	116.1 (2)
Mn–P–C11	122.0 (2)	C5–P–C11	103.7 (2)
Mn–C1–O1	176.6 (4)	Mn–C2–O2	178.3 (5)
Mn–C3–O3	177.6 (4)	Mn–C4–O4	177.6 (6)
P–C5–C6	120.4 (4)	P–C5–C10	120.6 (4)

the bromine and diphenylphosphine ligands cis to each other. The Mn–Br distance, 2.532 (1) Å, is very similar to those observed in $Mn(CO)_3Br\{P(OMe)_2Ph\}_2$[27] and $MnBr(CO)_3(CNPh)_2$.[28] The Mn–P bond length of 2.339 (1) Å also falls within the range of values described for Mn–terminal phosphine compounds,[25] although it is somewhat longer than those for 2 and 3. The two CO ligands trans to each other have very similar Mn–CO bond lengths of 1.877 (5) and 1.888 (5) Å, while those trans to bromine and the phosphine show shorter distances of 1.814 (6) and 1.831 (6) Å. This seems to reflect the fact that bromide and phosphine ligands would not compete nearly so much for π-back-bonding electron density as would another carbonyl ligand.

An attempt to determine the crystal structure of **8a** was also made. However, poor crystal quality precluded an accurate structural analysis. Only the octahedral coordination geometry of the metal atom, having a *fac* arrangement of the CO groups and a cis orientation of the diphenylphosphine ligands, could be determined.

Experimental Section

General Considerations. All manipulations were conducted under nitrogen by use of standard Schlenk techniques. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, and Oneida Research Services, Inc. Whitesboro, NY.

The solvents cyclohexane, hexane, diethyl ether, and tetrahydrofuran were dried with $LiAlH_4$ or sodium/benzophenone and distilled before use. Dichloromethane and chloroform were dried over calcium hydride and distilled. $C_5H_7Mn(CO)_3$,[5a] $C_5H_7SnBu_3$,[5a] $MnBr(CO)_4PHPh_2$,[8,29] and $MnBr(CO)_3(PHPh_2)_2$[8] were prepared according to reported procedures, while $PHPh_2$ was purchased from Aldrich.

Single-Crystal X-ray Diffraction Studies. Suitable crystals of **2**, **3**, and **7a** were mounted in glass capillaries under an inert atmosphere. The X-ray data collections, structure solutions, and refinements were carried out on a Nicolet R3m four-circle automatic diffractometer at room temperature using Cu Kα graphite-monochromated radiation (λ = 1.541 78 Å) and operated in the $\theta/2\theta$ scanning mode. The cell parameters were established by least-squares refinement of the setting angles of 25 strong machine-centered reflections. The crystal data and the details of the data collections and structure analyses are summarized in Table VIII. During the data collection two standard reflections were measured after every 46 reflections (98 for **2**) as check reflections to monitor crystal deterioration and/or misalignment. The measured data were corrected for background, Lorentz, and polarization effects as well as for absorption, for which the crystal was considered to have a pseudoellipsoid shape for **3** and **7a**, whereas that of **2** employed ψ scans. The coordinates of the manganese atoms were determined from Patterson syntheses and checked for **3** and **7a** by use of direct methods. All remaining non-hydrogen atoms were found after successive full-matrix least-squares refinements and difference Fourier map calculations. After anisotropic refinement of the non-hydrogen atoms, the hydrogen atoms were located in difference Fourier maps. Except for H2 and H3 for **3** and P–H for **7a**, the hydrogens were placed in idealized positions and were included in the structure factor calculations with fixed isotropic thermal parameters. The least-squares weighting scheme used was $w = 1/[\sigma^2(F_o) + G(F_o)^2]$, where σ is the standard deviation of the observed amplitudes based on counting statistics and G is a variable adjusted after each cycle to minimize the function $\sum w(\Delta F)^2$. In **2**, a fixed "ignorance factor" of 0.04 was employed. The final G value and other relevant refinement values are summarized in Table VIII. Some reflections were discarded to improve the final refinements.

The systematic absences for **2** were consistent with either $Pna2_1$ or $Pnma$, but the density of the crystal suggested it to be $Pna2_1$ as was further supported by the successful structure solution and refinements. In the cases of **3** and **7a**, the systematic absences were consistent with $P2_1/a$ and $P2_1/c$, respectively, also in agreement with the successful structure refinements.

Spectroscopic Studies. Infrared spectra were recorded on a Nicolet MX-1-FT spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300GS spectrometer, and chemical shifts are reported relative to internal Me_4Si. ^{31}P NMR spectra were recorded on a JEOL FX90Q spectrometer using H_3PO_4 (85%) as the external reference. Mass spectra were obtained by using a Hewlett-Packard 5985-A instrument operated at 70 eV.

Reaction of $C_5H_7Mn(CO)_3$ with $PHPh_2$. In a 150-mL two-necked flask equipped with a nitrogen inlet and stirring bar, 600 mg (2.91 mmol) of complex **1** was dissolved in 50 cm^3 of cyclohexane to give a pale yellow solution. $PHPh_2$ (0.54 g, 0.51 cm^3, 2.91 mmol) was added dropwise by syringe over ca. 1 min. The solution turned golden yellow after a few minutes of stirring at room temperature. A very air-sensitive yellow solid [mp 238–244 °C, dec; ^{31}P NMR (C_6D_6): δ 59 ppm (m)] precipitated. After 5 h the reaction was filtered and evaporated under vacuum to give a yellow oil which was recrystallized from hexane diethyl ether (9:1). Several recrystallizations allowed separation of the isomers,

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Table VIII. Crystallographic Data Summary

	2	3	7a
(1) Crystal Data			
cryst size, mm	0.36 × 0.24 × 0.18	0.60 × 0.60 × 0.30	0.08 × 0.25 × 0.50
stoichiometry	$C_{20}H_{18}MnO_3P$	$C_{20}H_{18}MnO_3P$	$C_{16}H_{11}BrMnO_4P$
mol wt	392.28	392.28	433.09
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$P2_1/a$	$P2_1/c$
a (Å)	8.844 (1)	10.630 (7)	11.325 (5)
b (Å)	16.806 (2)	11.979 (8)	10.342 (3)
c (Å)	12.629 (1)	14.27 (1)	14.813 (5)
β (deg)	90	92.32 (6)	95.08 (3)
V (Å^3)	1876.99	1851.81	1728.23
cryst color	yellow	light yellow	yellow
Z	4	4	4
T (K)	289	298	298
D_x (g cm^{-3})	1.388	1.398	1.653
F_{000}	1208.0	811.84	855.88
μ (Cu Kα, 1.54178 Å) (cm^{-1})	66.93	69.19	100.31
(2) Data Collection			
mode	θ–2θ	θ–2θ	θ–2θ
2θ limits (deg)	4–140	3–110	3–110
scan width, below Kα_1 (deg)	1.1	1.1	1.0
scan width, above Kα_2 (deg)	1.2	1.2	1.3
scan speed (variable) (deg min^{-1})	3.0	4.0–29.3	4.0–29.3
exposure time (h)		61.2	97.1
stability corr range on I	1.000–1.000	1.000–1.000	1.000–1.000
range in hkl min	0,0,–15	0,0,–16	0,0,–16
range in hkl max	10,20,0	12,13,16	13,11,16
calcd trans factors min, max (%)	52.00, 99.90	62.58, 99.99	54.15, 99.21
total no. of reflns colled	2076	2572	2449
no. of unique reflns [$I \geq 3\sigma(I)$]	1468	1940	2013
(3) Structure Refinement			
no. of reflns for final refinement	1468	1735	2001
no. of params refined	225	241	216
$R(F)$ (%)	5.96	6.41	4.95
R_w (%)	6.02	7.12	5.40
goodness of fit for last cycle	1.53	1.156	0.969
final g	^{a}	0.00458	0.00362
residual electron density (e Å^{-3})	0.92	0.62	0.74

^{a} An ignorance factor of 0.04 was used.

giving the less soluble complex **3** (114 mg, as a pale yellow solid, 10%) and 357 mg of **2** as a lemon yellow solid (31%).

[1-(Diphenylphosphino)-2–4-η^3-pentenyl]tricarbonylmanganese, $Mn[P(Ph)_2CH_2$-η^3-$CHCHCHCH_3](CO)_3$ (2). This compound was prepared as described above and isolated as a single isomer (see text). Mp: 126–127 °C. Anal. Calcd for $MnC_{20}H_{18}O_3P$: C, 61.22; H, 4.59. Found: C, 61.31; H, 4.65. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 2.0 (3 H, d, H5, J = 7 Hz), 2.75 (2 H, m, H1, H4, J = 7, 16.6 Hz), 3.30 (1 H, m, H4), 3.75 (1 H, m, H3), 4.45 (1 H, m, H2), 7.35–7.55 (10 H, m); (C_6D_6, 300 MHz) δ 2.08 (3 H, d, H5, J = 7 Hz), 2.43 (1 H, m, H4), 2.88 (2 H, m, H1, H4), 3.53 (1 H, m, H3), 4.43 (1 H, m, H2), 6.45 (6 H, s, br), 7.44 (4 H, d, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 20.8 (s, C5), 28.2 (d, C4, J_{PC} = 25 Hz), 46.3 (d, C3, J_{PC} = 16 Hz), 57.9 (s, C1), 99.1 (d, C2, J_{PC} = 4 Hz), 128.5 (d, C_m, J_{PC} = 10 Hz), 128.7 (d, C_m, J_{PC} = 9.2 Hz), 129.7 (s, C_p), 130.5 (s, C_p), 131.1 (d, C_o, J_{PC} = 10.3 Hz), 132.5 (d, C_o, J_{PC} = 11 Hz), 135.4 (d, C_i, J_{PC} = 38 Hz), 220, 225, 227 (br, CO). ^{13}C NMR (C_6D_6, 270 MHz): δ 21.0 (q, C5, J_{CH} = 127 Hz), 27.9 (t, C4, J_{CH} = 137 Hz), 46.9 (d, C3, J_{CH} = 163 Hz), 58.0 (d, C1, J_{CH} = 151 Hz), 99.2 (d, C2, J_{CH} = 155 Hz), 221, 225, 227 (br, CO). ^{31}P NMR ($CDCl_3$, 36.23 MHz): δ –25 (s, br). IR: (hexane) ν(CO) 2000, 1921, 1912 cm^{-1}; ($CHCl_3$) ν(CO) 1994, 1912, 1898 cm^{-1}. Mass spectrum (12 eV): m/e (relative intensity) 392 (11), 364 (1), 336 (15), 309 (21), 308 (100), 240 (45), 55 (<1).

[1-(Diphenylphosphino)-3–5-η^3-pentenyl]tricarbonylmanganese, $Mn[P(Ph)_2CH_2CH_2$-η^3-$CHCHCH_2](CO)_3$ (3). X-ray-quality crystals were formed by cooling a solution in the minimum amount of diethyl ether and hexane to 0 °C. Mp: 155–157 °C. Anal. Calcd for $MnC_{20}H_{18}O_3P$: C, 61.22; H, 4.59. Found: C, 61.33; H, 4.89. ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 1.30 (2 H, t, H1), 2.25 (1 H, m, H5), 2.40 (1 H, m, H5), 2.55 (1 H, s, br, H4), 2.8 (1 H, s, br, H4), 4.35 (1 H, m, H3), 4.82 (1 H, m, H2), 7.4 (6 H, s, br), 7.6 (4 H, m); (C_6D_6, 300 MHz) δ 1.40 (2 H, t, H1), 1.83 (1 H, m, H5), 1.97 (1 H, m, H5), 2.08 (1 H, m, H4), 2.79 (1 H, m, H4), 4.15 (1 H, m, H3), 4.82 (1 H, m, H2), 6.98–7.2 (8 H, m), 7.52 (1 H, m), 7.72 (1 H, t). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 25.6 (d, C4, J_{PC} = 15.1 Hz), 37.9 (d, C5, J = 22.1 Hz), 44.2 (s, C1), 74.8 (s, C3), 93.9 (s, C2), 128.7 (d, C_m, J_{PC} = 10.8 Hz), 128.8 (d, C_m, J_{PC} = 9.1 Hz), 129.9 (s, C_p), 130.1 (s, C_p), 131.3 (d, C_o, J_{PC} = 9.3 Hz), 132.0 (d, C_o, J_{PC} = 9.1 Hz), 133.2 (d, C_i, J_{PC} = 31.3 Hz), 136.2 (d, C_i, J_{PC} = 41.8 Hz). ^{31}P NMR ($CDCl_3$, 36.23 MHz): δ 76 (s, br). IR: (hexane) ν(CO) 2000, 1921, 1912 cm^{-1}; ($CHCl_3$) ν(CO) 1994, 1912, 1898 cm^{-1}. Mass spectrum (70 eV): m/e (relative intensity) 392 (8), 364 (1), 336 (7), 309 (22), 308 (100), 254 (50), 240 (34), 199 (18), 186 (10), 185 (23), 183 (36), 132 (33), 121 (18), 55 (45).

Reaction of *cis*-$MnBr(CO)_4PHPh_2$ with $C_5H_7SnBu_3$. To 0.50 g (1.15 mmol) of **7a** in 30 cm^3 of THF was added 0.412 g (0.34 cm^3, 1.15 mmol) of $C_5H_7SnBu_3$ at room temperature. The resulting solution was stirred for 4.5 h under reflux. The solvent was removed under reduced pressure, and the red-oil residue was dissolved in the minimum volume of diethyl ether and chromatographed on neutral alumina (70–230 ASM) by using petroleum ether or diethyl ether. The first band, eluted with petroleum ether, corresponded to complex **1** and recovered $C_5H_7SnBu_3$. The second band eluted with diethyl ether afforded 16 mg of complex **2** (6.6%).

Reaction of *fac*-$MnBr(CO)_3(PHPh_2)_2$ with $C_5H_7SnBu_3$. This reaction was carried out as above using a stoichiometric ratio of reactants (0.846 mmol), leading basically to recovered starting materials (see text) and a trace amount of complex **2**.

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Supplementary Material Available: Tables of atomic (hydrogen and non-hydrogen) coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors for 2, 3, and 7 and tables of torsion angles for 2 and 3 (16 pages). Ordering information is given on any current masthead page.

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Structural and Electrochemical Study of a 2,2′-Biphosphinine

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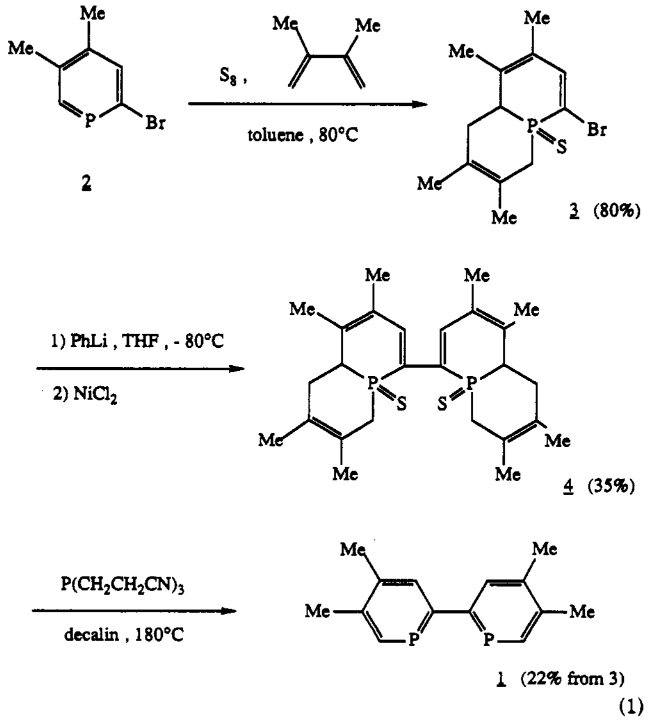
An improved synthesis of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine from 2-bromo-4,5-dimethylphosphinine using $(Ph_3P)_2CoCl_2$ as the coupling reagent is described. The coupling can also be effected in the coordination sphere of molybdenum tetracarbonyl via a bromine to lithium exchange followed by C–C bond formation with $(DME)NiBr_2$. The recovery of the free 2,2′-biphosphinine from the $Mo(CO)_4$ chelate thus obtained appears to be difficult. The X-ray crystal structure analysis of the 2,2′-biphosphinine at −100 °C suggests that the interaction between the two rings and the rotation barrier around the C–C bridge are weak. The complexation with $Cr(CO)_4$ does not alter the geometry of the biphosphinine, and no electronic delocalization seems to be operative within the five-membered metallacycle. The electrochemical reduction of the tetramethylbiphosphinine is easier than that of 4,4′-dimethyl-2,2′-bipyridine. The first monoelectronic wave occurs at -1.85_2 V vs SCE in DMF for the phosphorus ligand as compared to -2.20_1 V vs SCE for the nitrogen ligand. As a consequence, the 2,2′-biphosphinine is a better ligand for electron-rich metals and is able to displace 2,2′-bipyridine from its $Cr(CO)_4$ chelate.

In a recent communication,[1] we have described the synthesis of the first 2,2′-biphosphinine 1. As the phosphorus analogues of the well-known 2,2′-bipyridines, 2,2′-biphosphinines offer some interesting perspectives on coordination chemistry. Before undertaking the study of their transition-metal complexes, however, it was necessary to evaluate the structural requirements and the donor–acceptor capacity of this new class of chelating ligands. In this work, we describe several experiments aimed at the improvement of the synthesis of 1 together with its X-ray crystal structure analysis and a comparison of its electrochemical properties with those of a related 2,2′-bipyridine.

Results and Discussion

The synthesis of 1 as reported in our preliminary communication is depicted in eq 1. After protecting the reactive P=C double bond via a [2 + 4] cycloaddition, we performed a bromine to lithium exchange and subsequently coupled the resulting lithio derivative with nickel(II) chloride, thereby obtaining 4. A reductive [2 + 4] cycloreversion then led to the 2,2′-biphosphinine 1. The weak point of this scheme was clearly the coupling step, since other experiments demonstrated that the bromine to lithium exchange is instantaneous and almost quantitative.[2] Thus, we tried the several coupling reagents shown in eq 2 while retaining all other reagents and experimental conditions. Bis(triphenylphosphine)di-



$$3 \xrightarrow[\text{(3) P(CH}_2\text{CH}_2\text{CN)}_3\text{, decalin, 180 °C, 7 h}]{\text{(1) PhLi, THF, -80 °C (2) MX}_2\text{, -80 °C, room temp}} 1 \qquad (2)$$

MX_2 = $(Ph_3P)_2NiCl_2$ (25%), $(Bu_3P)_2NiCl_2$ (0%), $(DME)NiBr_2$ (30%), $CoCl_2$ (10%), $(Ph_3P)_2CoCl_2$ (48%)

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[1] Le Floch, P.; Carmichael, D.; Richard, L.; Mathey, F. *J. Am. Chem. Soc.* 1991, *113*, 667.

[2] Le Floch, P.; Carmichael, D.; Mathey, F. *Organometallics* 1991, *10*, 2432.

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