Reactivity of Bis(diphenylphosphino)methanide Complexes of Manganese(I) toward Halogens and Pseudohalogens

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C-Functionalized diphosphinomethanide and diphosphine ligands of formula $[(PPh_2)_2CX]^-$ and $[(PPh_2)_2C(X)(Y)]$ (X = I, CN, SCN, SePh, Y = H; X = Br, Y = H, Br), coordinated to manganese(I), have been prepared by reaction of the methanide complexes $[Mn(L)(CO)_3\{(PPh_2)_2CH\}]$ (L = CO, CN^{t}Bu) with the halogen and pseudohalogen molecules Br_2, I_2, BrCN, $(CN)_2$, $(SCN)_2$ and ISePh followed, when necessary, by the appropriate basic (KOH) or acidic (HBF_4) treatment.

Introduction

A rich chemistry has been developed around the reactivity of alkali-metal diphosphinomethanides with halides of many metallic and nonmetallic elements (MX_n).[1] This has led to the preparation of a number of diphosphinomethanide derivatives displaying remarkable features, such as a variety of coordination modes (mono-, bi-, and tridentate through the carbon and phosphorus donor atoms), high coordination numbers,[2] and the noteworthy stabilization of molecules with elements in low oxidation states, such as those of silicon(II).[3] However, as far as we know, the study of the reactivity of diphosphinomethanide anions with dihalogen molecules themselves (X_2) has been limited to the treatment of lithium bis(diphenylphosphino)methanide with iodine, leading to the formation of $PPh_2PCH{=}PPh_2PPh_2{=}CHPPh_2$, $(Ph_2P)_2C{=}PPh_2CH_2PPh_2$, and $(Ph_2P)_2CHCH(PPh_2)_2$, which result from P−P, P−C, and C−C coupling, respectively.[4,5] Curiously, no halogenation product was isolated from the above reaction. In relation to this, as we will describe throughout this paper, we have found that the reaction of bis(diphenylphosphino)methanide η^2(P,P′)-coordinated in manganese(I) carbonyl complexes toward dihalogens (Br_2 and I_2) takes place in a very different way, allowing the formation of new C-halogenated diphosphines derived from dppm, as a result of the chemoselective halogenation at the central carbon atom. We have also extended the study of the reactivity of coordinated diphosphinomethanides to pseudohalogen molecules such as BrCN, $(CN)_2$, $(SCN)_2$, and ISePh, which has led to the formation of the new functionalized diphosphinomethanide ligands $[(Ph_2P)_2CCN]^-$, $[(Ph_2P)_2CSCN]^-$, and $[(Ph_2P)_2CSePh]^-$ and their corresponding diphosphines $(Ph_2P)_2C(H)CN$, $(Ph_2P)_2C(H)SCN$, and $(Ph_2P)_2C(H)SePh$. Preliminary accounts of some of this work have been published.[6,7]

Results and Discussion

Reactions of $[Mn(CO)_4\{(Ph_2P)_2CH\}]$ (2a) and *fac*-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CH\}]$ (2b) with Dihalogens. The diphosphinomethanide derivatives **2a**,**b**, which were prepared from the corresponding cationic dppm complexes $[Mn(L)(CO)_3\{(Ph_2P)_2CH_2\}]ClO_4$ (**1a**, L = CO; **1b**, L = CN^{t}Bu) by treatment with KOH,[8] readily react with Br_2 or I_2 in CH_2Cl_2 to give $[Mn(L)(CO)_3\{(Ph_2P)_2C(H)X\}]X_3$ (**3a**, L = CO, X = Br; **3b**, L = CN^{t}Bu, X = Br; **3c**, L = CO, X = I; **3d**, L = CN^{t}Bu, X = I) (see Scheme 1). These compounds contain the new C-halogenated diphosphines $(PPh_2)_2C(H)X$, arising from the heterolytic cleavage of the X_2 molecules promoted by the methanide carbon atom. As the ligand $[(PPh_2)_2CH]^-$ in **2a**,**b** is strongly bonded to manganese through the phosphorus atoms, the halogenation reaction was chemoselective on the methanide carbon atom and did not take place to any extent on the phosphorus atoms,

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[2] (a) Karsch, H. H.; Ferazin, G.; Steigelmann, O.; Kooijman, H.; Hiller, W. *Angew. Chem., Int. Ed.. Engl.* **1993**, *32*, 1739. (b) Karsch, H. H.; Deubelly, B.; Keller, U.; Steigelmann, O.; Lachmann, J.; Müller, G. *Chem. Ber.* **1996**, *129*, 671.

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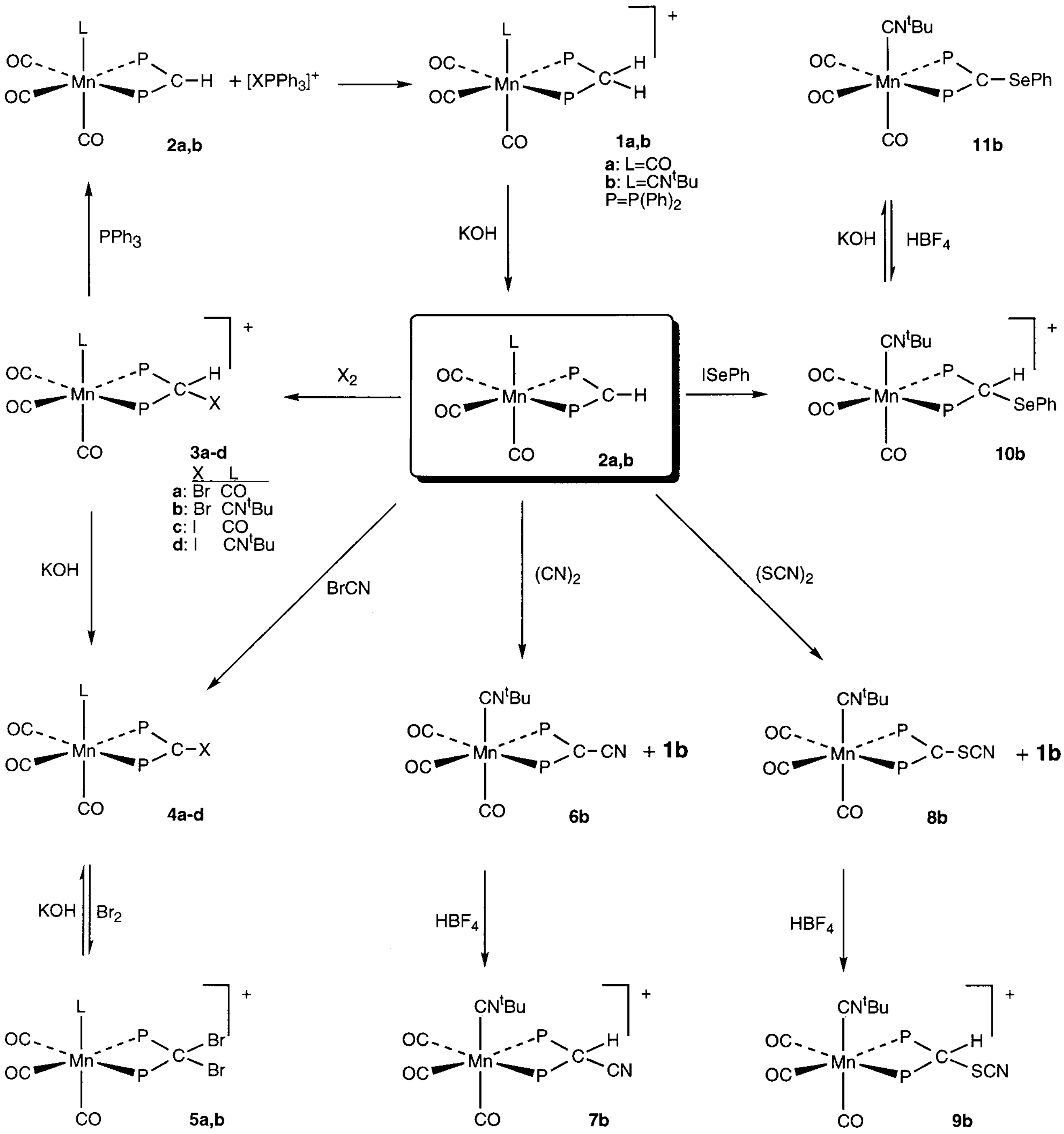
S0276-7333(98)00391-4 CCC: $15.00

Scheme 1



as does occur in free phosphines.[9] In contrast with that found by Braunstein et al. in the treatment of Li[$(PPh_2)_2CH$] with I_2,[5] we have not detected in the present reactions any product of oxidative C–C coupling. These authors have proposed that the formation of the tetraphosphine $(Ph_2P)_2CHCH(PPh_2)_2$ in the above reaction takes place through the radical intermediate $[(PPh_2)_2CH]^\bullet$ rather than through a metal–halogen exchange. We think, however, that this last pathway cannot be excluded in view of the formation of $[(PPh_2)_2C(H)X]$ in our synthetic approach.

It must be noted that, in these reactions, an excess of dihalogen must be employed in order to avoid the formation of a mixture containing, in addition to **3a**–**d**, some amount of **1a**–**d** and $[Mn(L)(CO)_3\{(Ph_2P)_2CX\}]$ (**4a**–**d**) (see below) due to proton migration from **3** to **2**. The presence of an excess of X_2 is the reason in every case the counteranion is the species X_3^- and not the monoatomic anion X^-, first formed in the heterolytic cleavage of the X_2 molecule by the diphosphinomethanide ligand.

For **3b**,**d** (L = CN^{t}Bu) two isomers are possible, depending upon whether the arrangement of the halogen on the central carbon atom is syn or anti with respect to the isocyanide ligand. The ^{1}H NMR data showed that both isomers are present in the reaction mixture, as revealed by the appearance of two triplets at about δ 6 for the $P_2C(H)X$ protons and of two ^{t}Bu singlets (see Table 1). However, when a solution of compound **3b** or **3d** in CH_2Cl_2 was set aside at room

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[9] du Mont, W. W.; Batcher, M.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 912.

Table 1. Selected Spectroscopic Data for the New Compounds

compd	ν_{CO}[a]	ν_{CN}[a]	^1H NMR[b]	$^{31}P\{^1H\}$ NMR[b]	$^{13}C\ \{^1H\}$ NMR[b]
$[Mn(CO)_4\{(Ph_2P)_2C(H)Br\}]Br_3$ (**3a**)	2097 s, 2038 m, 2016 vs		6.23 (t, P_2CHBr, $^2J_{PH} = 10$)	41.0 (s, br)	43.7 (t, P_2C, $^1J_{PC} = 10$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2C(H)Br\}]Br_3$ (**3b**)	2049 s, 1989 s	2180 m	0.95 (s, CN^tBu), 6.04 (t, P_2CHBr, $^2J_{PH} = 10$)[c]	45.3 (s, br)	43.1 (t, P_2C, $^1J_{PC} = 8$)
$[Mn(CO)_4\{(Ph_2P)_2C(H)I\}]I_3$ (**3c**)	2096 s, 2037 m, 2015 vs		6.46 (t, P_2CHI, $^2J_{PH} = 11$)	33.0 (s, br)	15.2 (t, P_2C, $^1J_{PC} = 10$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2C(H)I\}]I_3$ (**3d**)	2047 s, 1988 s	2180 m	0.87 (s, CN^tBu), 6.07 (t, P_2CHI, $^2J_{PH} = 11$)[c]	37.3 (s, br)	14.5 (t, P_2C, $^1J_{PC} = 7$)
$[Mn(CO)_4\{(Ph_2P)_2CBr\}]$ (**4a**)	2075 s, 1995 vs, 1965 s			10.1 (s, vbr)	1.2 (t, P_2C, $^1J_{PC} = 50$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CBr\}]$ (**4b**)	2017 vs, 1953 s, 1936 s	2174 m	0.71 (s, CN^tBu)	16.7 (s, br)	1.0 (t, P_2C, $^1J_{PC} = 46$)
$[Mn(CO)_4\{(Ph_2P)_2Cl\}]$ (**4c**)	2074 s, 1993 vs, 1965 s			5.2 (s, br)	−34.7 (t, P_2C, $^1J_{PC} = 46$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2Cl\}]$ (**4d**)	2016 vs, 1951 s, 1937 s	2173 m	0.73 (s, CN^tBu)	12.1 (s, br)	−35.3 (t, P_2C, $^1J_{PC} = 50$)
$[Mn(CO)_4\{(Ph_2P)_2CBr_2\}]Br_3$ (**5a**)	2100 s, 2041 m, 2025 vs			75.0 (s, br)	64.4 (t, P_2C , $^1J_{PC} = 3$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CBr_2\}]Br_3$(**5b**)	2051 s, 1993 s	2184 m	1.17 (s, CN^tBu)	81.7 (s, br)	64.8 (t, P_2C, $^1J_{PC} = 7$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CCN\}]$ (**6b**)	2023 s, 1960 s, 1945 s	2177 m, 2143 m	0.67(s, CN^tBu)	10.6 (s, br)	17.7 (t, P_2C, $^1J_{PC} = 56$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2C(H)CN\}]BF_4$ (**7b**)	2052 s, 1992 s	2240 w, 2182 m	0.88 (s, CN^tBu),[c] 6.53 (t, P_2CH, $^2J_{PH} = 11$)[d]	35.5 (s, br)[d]	
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CSCN\}]$ (**8b**)	2020 s, 1955 s, 1944 s	2174 m, 2135 w	0.77 (s, CN^tBu)	30.9 (s, br)	12.7 (t, P_2C, $^1J_{PC} = 44$), 117.2 (t, SCN, $^3J_{PC} = 4$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2C(H)SCN\}]BF_4$ (**9b**)	2051 s, 1992 s	2181 m, 2159 w	0.85 (s, CN^tBu),[c] 6.39 (t, P_2CH, $^2J_{PH} = 10$)[d]	48.1 (s, br)[d]	48.5 (t, P_2C, $^1J_{PC} = 9$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2C(H)SePh\}]BF_4$ (**10b**)	2045 s, 1984 s	2178 m	1.22 (s, CN^tBu),[c] 5.59 (t, P_2CH, $^2J_{PH} = 12$)[d]	44.9 (s, br)[d]	59.0 (t, P_2C, $^1J_{PC} = 10$)
fac-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CSePh\}]$ (**11b**)	2015 s, 1951 s, 1935 s	2169 m	0.89 (s, CN^tBu)	18.1 (s, br)	17.3 (t, P_2C, $^1J_{PC} = 40$)

[a] In units of cm^{-1} (measured in CH_2Cl_2). Abbreviations: v = very, s = strong, m = medium, w = weak. [b] Chemical shifts (δ) in ppm (measured in CD_2Cl_2); coupling constants in Hz. Abbreviations: s = singlet, t = triplet, br = broad. [c] These data correspond to the *anti* isomers (see text). Data for the *syn* isomers are as follows: **3b**, 1.15 (s, CN^tBu), 6.11 (t, P_2CHBr, $^2J_{PH} = 10$); **3d**, 1.11 (s, CN^tBu), 6.09 (t, P_2CHBr, $^2J_{PH} = 11$); **7b**, 1.18 (s, CN^tBu), 6.98 (t, P_2CH, $^2J_{PH} = 9$); **9b**, 0.99 (s, CN^tBu), 6.23 (t, P_2CH, $^2J_{PH} = 10$); **10b**, 0.92 (s, CN^tBu), 5.74 (t, P_2CH, $^2J_{PH} = 12$). [d] In $CDCl_3$.

temperature, successive proton spectra showed slow conversion from one isomer to the other. After several days, only one isomer was present, which could be the one with the halogen arranged anti with respect to the bulky CN^tBu ligand. To confirm this and to gain knowledge about the structural data of the new diphosphine, an X-ray diffraction study was carried out for **3b**. A view of the complex cation is depicted in Figure 1, showing the manganese in a distorted-octahedral coordination geometry. As was anticipated, the bromine atom is located anti with respect to the isocyanide ligand, this being due apparently to steric reasons. The C(1)−Br(1) bond length (1.98(1) Å) is typical of bromoalkanes,[10] and the P(1)−C(1) (1.82(1) Å) and P(2)−C(1) (1.83(1) Å) distances are of the same order as those usually found in dppm derivatives (single bond P−C). These data are consistent with a sp^3 hybridization for carbon C(1), although the bond angles around this atom (P(1)−C(1)−P(2) = 99.0(4)°, P(1)−C(1)−Br(1) = 120.0(5)°, P(2)−C(1)−Br(1) = 121.4(5)°) indicate a strongly distorted tetrahedral coordination geometry, arising from the strain introduced by the small bite angle of the diphosphine and from the different size and nature of the carbon substituents.

The diphosphines $(PPh_2)_2C(H)X$ in complexes **3a**−**d** are able to react with bases in two different ways. In fact the experiments show that both substituents at the central carbon atom, hydrogen and halogen, are electrophilic in character and can be abstracted as H^+ or X^+ depending upon the nature of the nucleophile used. Thus, the reaction of a dichloromethane solution of **3a**−**d** toward a hard nucleophile such as OH^- (from

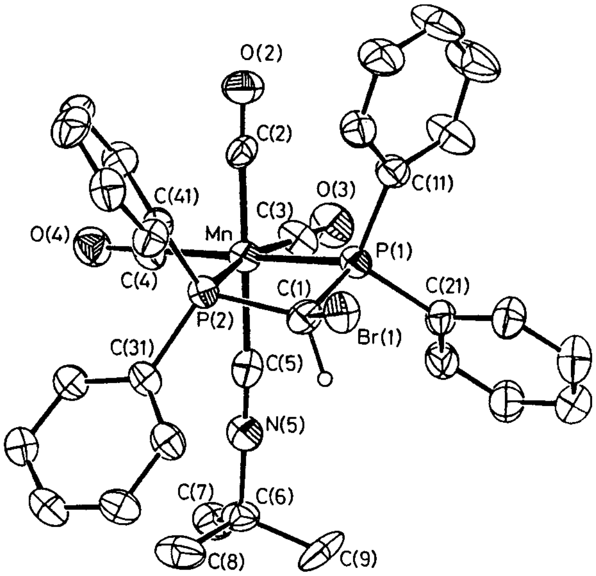

Figure 1. X-ray structure of the cation of **3b**, *fac*-$[Mn(CN^tBu)(CO)_3\{(PPh_2)_2C(H)Br\}]^+$, showing 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): C(1)−Br(1) = 1.98(1), P(1)−C(1) = 1.82(1), P(2)−C(1) = 1.83(1), Mn−P(1) = 2.299(5), Mn−P(2) = 2.341(4); P(1)−C(1)−P(2) = 99.0(4), P(1)−C(1)−Br(1) = 120.0(5), P(2)−C(1)−Br(1) = 121.4(5), P(1)−Mn−P(2) = 73.6(2).

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KOH) takes place with proton abstraction, leading to the formation of [Mn(L)(CO)$_3${(Ph$_2$P)$_2$CX}] (**4a**−**d**). However, when a soft nucleophile such as PPh$_3$ is employed, dehalogenation of the diphosphine immediately occurs to give finally [Mn(L)(CO)$_3${(Ph$_2$P)$_2$CH$_2$}]$^+$ (**1a**−**d**). As shown in Scheme 1, we propose for this last reaction a mechanism involving, in a first step, the formation of [Mn(L)(CO)$_3${(Ph$_2$P)$_2$CH}] (**2a**−**d**) and the phosphonium cation [XPPh$_3$]$^+$, which is acidic enough to protonate **2a**−**d**, affording **1a**−**d**. Supporting this, in an independent experiment we have proved that a dichloromethane solution of **2b** readily reacts with freshly prepared [IPPh$_3$]$^+$I$^-$,[11] affording **1b**, in addition to other phosphorus-containing species which so far remain uncharacterized.

In the ^{13}C{^{1}H} NMR spectra of **4a**−**d** the resonances for the P$_2$CX carbon atoms appear at remarkably high fields (see Table 1), and the values of $^1J_{PC}$ (about 50 Hz) are much higher than those in **3a**−**d** (about 10 Hz), owing to the higher degree of s character of the central carbon atom in **4** (sp^2) compared to that in **3** (sp^3).[12]

Although complexes of type **4** are less reactive than **2** toward electrophilic agents, in some cases they are still able to react properly with dihalogen molecules. Thus, the treatment of **4a**,**b** with Br$_2$ in CH$_2$Cl$_2$ causes another heterolytic cleavage of the dihalogen to give the cationic complexes [Mn(L)(CO)$_3${(Ph$_2$P)$_2$CBr$_2$}]Br$_3$ (**5a**,**b**). In contrast, the reaction of **4c**,**d** with I$_2$ in CH$_2$Cl$_2$ gave an intractable mixture of species, the spectroscopic data of which indicate that double C-iodination of the diphosphine might occur, but only partially. In **5a**,**b** the bromine atoms of the diphosphine are electrophilic, as is proved by their reaction with KOH to afford **4a**,**b**. It must be noted that the diphosphine [(Ph$_2$P)$_2$CBr$_2$] is a curious example of a molecule containing a tetrahedral carbon atom only surrounded by heteroatoms (core P$_2$-CBr$_2$).

Reactions of *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CH}] (2b) with Pseudohalogens. In the search for new types of functionalized diphosphines and in view of the reactivity of the methanide derivatives **2a**,**b** toward dihalogens, we extended the study of this reactivity to di-pseudohalogen molecules, such as (CN)$_2$, BrCN, (SCN)$_2$, and ISePh. We have found that these molecules undergo heterolytic cleavage of C−C, Br−C, S−S, and I−Se bonds, respectively.

The reaction of **2b** with cyanogen leads to the formation of *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CCN}] (**6b**) together with an equivalent amount of the dppm derivative *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CH$_2$}]$^+$ (**1b**) (see Scheme 1). Both complexes are easily separated by column chromatography. On the basis of that found in the reaction of **2b** with dihalogens, we propose that the present reaction takes place through the formation of the cationic intermediate *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C-(H)CN}]$^+$ (**7b**) (which is comparable to complexes of type **3**), in which the highly acidic character of the P$_2$C(H)-CN hydrogen promotes a proton transfer to **2b**, affording the final observed mixture. In fact, the reaction of **6b** with an excess of HBF$_4$ in CH$_2$Cl$_2$ led to the formation of **7b**, which has been spectroscopically characterized but not isolated as a pure compound because it slowly changes to **6b** on removing the excess acid. The IR spectrum of **6b** in CH$_2$Cl$_2$, in the region 2200−1800 cm^{-1}, shows, in addition to the ν_{CO} and ν_{CN} bands of carbonyls and isocyanide, a new ν_{CN} absorption at 2143 cm^{-1} corresponding to the cyano substituent of the methanide. As far as we know, the only complex that has been described previously containing a cyano−diphosphinomethanide ligand is the dinuclear species [Fe$_2$(CO)$_6$(μ-PPh$_2$){η^2-(P,P')-μ-(PPh$_2$)$_2$CCN}],[13] which was formed in a rather unexpected way.

The reaction of **2b** with BrCN yields directly the bromination product **4b** and not the cyanation product **6b**. In fact, this is a clean one-step synthetic procedure for obtaining **4b**. Basically, this result can be rationalized by assuming a Br$^{\delta+}$CN$^{\delta-}$ charge distribution for this reagent, which forces the nucleophilic attack of the methanide to take place on the bromine atom.

The methanide complex **2b** was also able to react under mild conditions with thiocyanogen, (SCN)$_2$, affording a mixture of the new thiocyanate−diphosphinomethanide derivative *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$-CSCN}] (**8b**) and the starting dppm complex **1b**. After column chromatography, **8b** was isolated as colorless crystals. Its spectroscopic data are consistent with a thiocyanate structure for the new ligand, [(Ph$_2$P)$_2$-CSCN]$^-$, rather than its isomeric isothiocyanate form [(Ph$_2$P)$_2$CNCS]$^-$. Thus, the IR spectrum of **8b** shows a sharp band at 2135 cm^{-1}, which is in the range corresponding to organic thiocyanates.[14] Furthermore, in the ^{13}C{^{1}H} NMR spectrum, the resonance of the −SCN carbon appears as a triplet at δ 117.2 ($^3J_{PC}$ = 4 Hz).[14] **8b** readily reacts with HBF$_4$ to give the cationic complex *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)SCN}]$^+$ (**9b**), which should be the intermediate species in the formation of **8b**. This was stable enough to be isolated as a white solid, which was fully characterized (see Table 1 and Experimental Section).

Finally, the reaction of **2b** with ISePh promotes the heterolytic cleavage of the I−Se bond to give a mixture of *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)SePh}]$^+$ (**10b**), *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CSePh}] (**11b**), and **1b**. After treatment with KOH and further column chromatography, **11b** was isolated as a white solid in 80% yield. As expected, a protonation reaction carried out on **11b** with HBF$_4$ afforded **10b**.

A general consideration to be made regarding all the cationic species *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)CN}]$^+$ (**7b**), *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)SCN}]$^+$ (**9b**), and *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)SePh}]$^+$ (**10b**) is that they appear as a mixture of two isomers, arising from the relative syn and anti dispositions of the substituent CN, SCN, or SePh of the diphosphine, with respect to the CN^{t}Bu ligand. This is shown by the spectroscopic data of these complexes (see Table 1), especially by the appearance of two P$_2$C(H)− triplets at about δ 6.5 and two CN^{t}Bu resonances in the proton spectra. However, when it stands in CH$_2$Cl$_2$ at room

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temperature, the mixture slowly changes to one isomer only, which should be the anti one on the basis of the structure found for the very similar complex **3b** (see above).

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Solvents were dried and purified by standard techniques and distilled under nitrogen prior to use. All reactions were monitored by IR spectroscopy (Perkin-Elmer FT 1720-X and Paragon 1000 spectrophotometers). The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with Bruker AC-300 and AC-200 instruments. Chemical shifts are given in ppm, relative to internal SiMe$_4$ (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). The complexes [Mn(CO)$_4${(Ph$_2$P)$_2$CH}] (**2a**) and *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CH}] (**2b**)[8] and the reagents (CN)$_2$[15] and (SCN)$_2$[16] were prepared as described elsewhere. All other reagents were commercially obtained and were used without further purification.

[Mn(CO)$_4${(Ph$_2$P)$_2$C(H)Br}]Br$_3$ (3a). A solution of [Mn(CO)$_4${(Ph$_2$P)$_2$CH}] (**2a**; 0.20 g, 0.36 mmol) in 20 mL of CH$_2$Cl$_2$ was added dropwise to an excess of bromine (0.13 mL, 2.54 mmol) at room temperature with continuous stirring. The solvent was then evaporated to dryness and the residue washed with hexane (30 mL) and dried under vacuum. A yellow crystalline solid was obtained (0.30 g, 96%). The product can be recrystallized from CH$_2$Cl$_2$/hexane. Anal. Calcd for $C_{29}H_{21}Br_4MnO_4P_2$: C, 40.04; H, 2.43. Found: C, 40.37; H, 2.34.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)Br}]Br$_3$ (3b).** The procedure is completely analogous to that described above, using *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CH}] (**2b**; 0.20 g, 0.33 mmol) and Br$_2$ (0.12 mL, 2.31 mmol). Yield: 0.26 g (85%). Anal. Calcd for $C_{33}H_{30}Br_4MnNO_3P_2$: C, 42.84; H, 3.27; N, 1.51. Found: C, 42.97; H, 3.24; N, 1.46. Slow diffusion of hexane into a CH$_2$Cl$_2$ solution of the compound afforded yellow crystals suitable for X-ray diffraction study.

[Mn(CO)$_4${(Ph$_2$P)$_2$C(H)I}]I$_3$ (3c). This was similarly prepared from **2a** (0.20 g, 0.36 mmol) and I$_2$ (0.64 g, 2.54 mmol): red crystals from CH$_2$Cl$_2$/hexane. Yield: 0.29 g (76%). Anal. Calcd for $C_{29}H_{21}I_4MnO_4P_2$: C, 32.92; H, 2.00. Found: C, 32.71; H, 1.93.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)I}]I$_3$ (3d).** This was similarly prepared from **2b** (0.20 g, 0.33 mmol) and I$_2$ (0.59 g, 2.32 mmol): brown-red solid. Yield: 0.26 g (70%). Anal. Calcd for $C_{33}H_{30}I_4MnNO_3P_2$: C, 35.61; H, 2.72; N, 1.26. Found: C, 35.73; H, 2.68; N, 1.30.

[Mn(CO)$_4${(Ph$_2$P)$_2$CBr}] (4a). An excess of KOH (1 g) was added to a solution of **3a** (0.2 g, 0.23 mmol) in 20 mL of CH$_2$Cl$_2$. The mixture was stirred until the IR spectrum of the solution showed no bands corresponding to **3a** (2 h approximately). The resulting yellow solution was filtered off and concentrated to 5 mL. Addition of hexane and cooling (−20 °C) gave yellow crystals of the product. Yield: 0.12 g (83%). Anal. Calcd for $C_{29}H_{20}BrMnO_4P_2$: C, 55,35; H, 3.20. Found: C, 55.31; H, 3.20.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CBr}] (4b).** The procedure is completely analogous to that described above, using **3b** (0.25 g, 0.27 mmol) and KOH (1 g). Yield: 0.18 g (90%). Anal. Calcd for $C_{33}H_{29}BrMnNO_3P_2$: C, 57,91; H, 2.05; N, 4.27. Found: C, 57.84; H, 2.15; N, 4.27.

[Mn(CO)$_4${(Ph$_2$P)$_2$CI}] (4c). This was similarly prepared from **3c** (0.15 g, 0.14 mmol). Yield: 77 mg (81%). Anal. Calcd for $C_{29}H_{20}IMnO_4P_2$: C, 51.51; H, 2.98. Found: C, 51.23; H, 2.80. Pale yellow crystals of **4c·CH$_2$Cl$_2$**, suitable for X-ray diffraction study, were obtained by recrystallization from CH$_2$Cl$_2$/hexane.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CI}] (4d).** This was similarly prepared from **3d** (0.25 g, 0.22 mmol) and KOH (1 g). Yield: 0.15 g (90%). Anal. Calcd for $C_{33}H_{29}IMnNO_3P_2$: C, 54.19; H, 1.91; N, 4.00. Found: C, 54.01; H, 1.94; N, 3.99.

[Mn(CO)$_4${(Ph$_2$P)$_2$CBr$_2$}]Br$_3$ (5a). A solution of **4a** (0.15 g, 0.24 mmol) in 20 mL of CH$_2$Cl$_2$ was added dropwise to an excess of bromine (61 μL, 1.18 mmol). The resulting mixture was stirred for 10 min. The solvent was then evaporated to dryness under reduced pressure. The residue was washed with hexane (20 mL), giving a yellow solid (0.21 g, 93%). The product can be recystallized from CH$_2$Cl$_2$/hexane. Anal. Calcd for $C_{29}H_{20}Br_5MnO_4P_2$: C, 36.71; H, 2.12. Found: C, 36.51; H, 2.08.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CBr$_2$}]Br$_3$ (5b).** This was similarly prepared from **4b** (0.20 g, 0.29 mmol) and Br$_2$ (80 μL, 1.55 mmol). Anal. Calcd for $C_{33}H_{29}Br_5MnNO_3P_2$: C, 39.48; H, 2.91; N, 1.39. Found: C, 39.57; H, 2.95; N, 1.41.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CCN}] (6b).** To a solution of **2b** (0.30 g, 0.49 mmol) in CH$_2$Cl$_2$ (25 mL), (CN)$_2$ was bubbled through. The reaction was monitored by IR spectroscopy, until all the starting material had been consumed (about 1 h). Bands corresponding to **1b** and **6b** were observed. The solution was then evaporated to dryness and the remaining solid chromatographed through an alumina column (activity III). Elution with CH$_2$Cl$_2$/hexane (1:2) and evaporation of the solvent give the desired product **6b** as a white solid. Yield: 0.11 g (35%). Anal. Calcd for $C_{34}H_{29}MnN_2O_3P_2$: C, 64.77; H, 4.63; N, 4.44. Found: C, 64.73; H, 4.64; N, 4.13.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CSCN}] (8b).** To a solution of **2b** (0.35 g, 0.58 mmol) in 15 mL of CH$_2$Cl$_2$ was added a solution containing (SCN)$_2$ (45 mg, 0.38 mmol) in 15 mL of CH$_2$Cl$_2$ dropwise with continuous stirring. The reaction occurs instantaneously, giving a mixture of **1b** and **8b** (by IR spectroscopy). The solution was then evaporated to dryness and the remaining solid chromatographed through an alumina column (activity III). Elution with CH$_2$Cl$_2$/hexane (1:2) and evaporation of the solvent give **8b** as a white solid. Yield: 0.13 g (34%). Anal. Calcd for $C_{34}H_{29}MnN_2O_3P_2S$: C, 61.64; H, 4.41; N, 4.23. Found: 61.33; H, 4.35; N, 4.12.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)SCN}]BF$_4$ (9b).** To a solution of **8b** (0.1 g, 0.15 mmol) in 15 mL of CH$_2$Cl$_2$ was added tetrafluoroboric acid−diethyl ether complex (85%; 52 μL, 0.30 mmol) with stirring. The formation of **9b** takes place instantaneously. The solvent was then evaporated to dryness and the residue washed with diethyl ether (3 × 5 mL). A white solid was formed, which was recrystallized from CH$_2$Cl$_2$/hexane. Yield: 96 mg (85%). Anal. Calcd for $C_{34}H_{30}BF_4MnN_2O_3P_2S$: C, 54.42; H, 4.03; N, 3.73. Found: C, 54.63; H, 4.20; N, 3.60.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CSePh}] (11b).** A solution of **2b** (0.2 g, 0.33 mmol) in 20 mL of CH$_2$Cl$_2$ was added dropwise to ISePh (93 mg, 33 mmol) with continuous stirring. Once the addition was finished, the resulting mixture was treated with an excess of KOH (1 g) and stirred for 30 min. The solution was filtered off and evaporated to dryness to give a pale yellow residue. This was chromatographed through an alumina column (activity III), using CH$_2$Cl$_2$/hexane (1:1) as eluent. Evaporation of the solvent to dryness gave **11b** as a white solid. Yield: 0.20 g (80%). Anal. Calcd for $C_{39}H_{34}MnNO_3P_2Se$: C, 61.59; H, 4.50; N, 1.84. Found: C, 61.11; H, 4.58; N, 1.89.

***fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$C(H)SePh}]BF$_4$ (10b).** This was prepared similarly to **9b**, starting from **11b** (0.10 g, 0.13 mmol) and HBF$_4$·Et$_2$O (85%, 45 μL, 0.26 mmol). Yield: 89 mg (80%). Anal. Calcd for $C_{39}H_{35}BF_4MnNO_3P_2Se$: C, 55.21; H, 4.16; N, 1.65. Found: C, 55.45; H, 4.28; N, 1.54.

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Table 2. Summary of Crystallographic Data

compd	**3b**
emp formula	$C_{33}H_{30}Br_4MnNO_3P_2$
fw	925.10
cryst syst	monoclinic
space group	$C2/c$
a (Å)	32.76(8)
b (Å)	11.236(2)
c (Å)	21.195(3)
α (deg)	90
β (deg)	110.99(7)
γ (deg)	90
V (Å^3)	7286(18)
Z	8
d(calcd) (g/cm^3)	1.687
μ (mm^{-1})	4.870
T, K	293(2)
wavelength (Å)	0.710 73
diffractometer	CAD4 Nonius
θ range (deg)	1.33−22.99
residuals: R1;[a] wR2[b]	0.0548; 0.1631
goodness of fit	0.905
$(\Delta/\sigma)_{\min}$ (e Å^{-3})	−0.732
$(\Delta/\sigma)_{\max}$ (e Å^{-3})	0.684

[a] $R1 = \sum|\Delta F|/\sum|F_o|$. [b] $wR2 = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2}$.

X-ray Crystallography. Crystals of **3b** suitable for X-ray diffraction analysis were grown from a dichloromethane solution layered with hexane at 25 °C. Data collection, crystal, and refinement parameters are summarized in Table 2. Unit cell parameters were obtained from the least-squares fit of 25 reflections with θ between 9 and 12°. Lorentz and polarization corrections were applied. The structures were solved by direct methods using SHELXS86[17] and expanded by DIRDIF.[18] Isotropic full-matrix least-squares refinement on F using SHELX76[19] converged to $R = 0.17$. At this stage additional empirical absorption correction was performed using DIFABS.[20] Maximum and minimum correction factors were 1.00 and 0.35, respectively. All non-hydrogen atoms were anisotropically refined on F^2 using SHELXL93.[21] The drawing of the complex shown in Figure 1 was made using EUCLID.[22]

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Supporting Information Available: Text giving details of the crystal data and tables of crystal data, atomic coordinates and U_{eq} values, interatomic distances and angles, and anisotropic displacement parameters for **3b** (8 pages). Ordering information is given on any current masthead page.

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