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Cyanogen Activation by Coordinated Bis(diphenylphosphino)methanide. The Ligand [(PPh$_2$)$_2$CCN]$^-$ as a Building Block in the Synthesis of Heterometallic Complexes

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*Summary: The new cyanodiphosphinomethanide complex fac-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$CCN}] (**2**) has been prepared by treatment of fac-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$CH}] (**1**) with cyanogen. **2** has shown to be a valuable substrate for the synthesis of heterometallic species; thus, by coordination of some additional metallic fragments through the free nitrogen atom of the cyano group, the new heterometallic complexes fac-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CCNAuPPh$_3$}]PF$_6$ (**5**) and fac-[{Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CCN}}$_2$Cu]BF$_4$ (**6**) have been obtained.*

The study of the reactivity of η^2-(P,P′)-coordinated diphosphinomethanide ligands ([R$_2$PC(H)PR$_2$]$^-$) has been mainly directed toward the synthesis of heterometallic complexes, making use of the ability of these groups to act as tridentate ligands, through the two phosphorus atoms and the central carbon atom.[1] The reactivity of these coordinated methanide ligands with nonmetallic electrophilic reagents has been less studied,[2] despite its potential application for the synthesis of new diphosphines. In this context, we have recently reported that the treatment of [Mn(CO)$_4${(PPh$_2$)$_2$CH}] with dihalogen molecules yields the new diphosphine and diphosphinomethanide ligands (PPh$_2$)$_2$CH(X), (PPh$_2$)$_2$CX$_2$, and [(PPh$_2$)$_2$CX]$^-$ (X = Br, I), coordinated to manganese(I).[3] Bearing in mind the pseudohalogen character of the CN group, we have now found an easy way to introduce a cyano functionality at the central carbon atom of diphosphinomethanides, by reaction with cyanogen.

As shown in Scheme 1, the treatment of neutral *fac*-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$CH}] (**1**) with an excess of cyanogen yields the new cyanodiphosphinomethanide derivative *fac*-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$CCN}] (**2**),[4] together with an equivalent amount of *fac*-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$CH$_2$}]$^+$ (**3**), which is the cationic precursor of **1** with chelated dppm.[1b] Complex **2** can be easily separated from **3** by column chromatography.[4]

To our knowledge, the only complex so far described in the literature containing the anionic ligand [(PPh$_2$)$_2$-

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

[1] See for instance: (a) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743. (b) Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; García-Fernández, A. *Organometallics* **1992**, *11*, 4077. (c) Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Pérez-Carreño, E. *J. Chem. Soc., Chem. Commun.* **1993**, *9*, 740 and references therein.

[2] (a) Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *74*, 235. (b) Al-Jibori, S.; Hall, M.; Hutton, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863.

[3] Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Menéndez-Velázquez, A. *Organometallics* **1994**, *13*, 4162.

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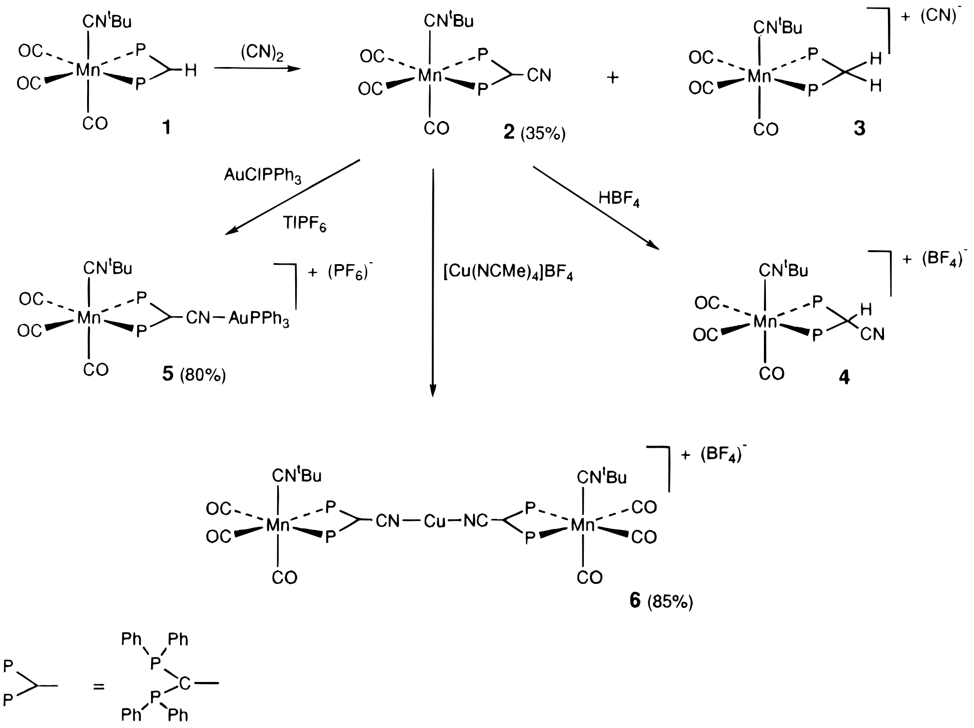
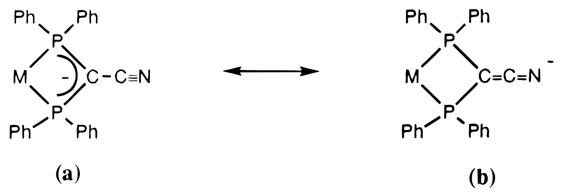
Scheme 1



CCN]$^-$ is the dinuclear species [Fe$_2$(CO)$_6$(μ-PPh$_2$){η^2-(P,P')-μ-(PPh$_2$)$_2$CCN}],[5] in which the new ligand was formed in a rather serendipitous way.

Complex **2** has been fully spectroscopically characterized.[6] Of note is the presence of a band at 2143 cm^{-1} in its infrared spectrum, corresponding to the ν(CN) vibration of the cyano group.

To explain the obtention of a mixture of **2** and **3** in this reaction, it seems reasonable to propose the formation, in a previous step, of the ionic intermediate *fac*-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$C(H)CN}]$^+$(CN)$^-$ (**4-CN**), which arises from a heterolytic cleavage of the cyanogen molecule. In this intermediate the P$_2$C(H)(CN) proton should have an enhanced acidic character, due to the high electronegativity of the CN substituent, and could be transferred to another molecule of **1**, giving the final observed mixture. In agreement with this interpretation, in the treatment of **2** with an excess of HBF$_4$ in CH$_2$Cl$_2$ as solvent, a complex which appears to be the proposed cationic intermediate **4** (obviously with BF$_4^-$ as counteranion) was spectroscopically detected.[7] However, we have not been able to isolate **4-BF$_4$** as a pure sample, because it slowly changes to **2** by removing the excess of acid (for instance on washing with Et$_2$O). This result is an indication of the high acidic character of the P$_2$C(H)CN proton in **4**.



(a) (b)

Figure 1.

Cyanogen bromide was also checked as a cyanation agent for **1**, but in this case only the bromination process takes place to give *fac*-[Mn(CN^{t}Bu)(CO)$_3${(PPh$_2$)$_2$CBr}], a complex already prepared by us in a different way.[3]

Looking to the two simple forms for the bond description of the new ligand in **2** (see Figure 1), it seems clear that this ligand has some additional coordination ability, either through the methanide carbon or through the nitrogen atom, thus being a promising substrate for the synthesis of heterometallic species. Effectually, as shown in Scheme 1, we have been able to coordinate this ligand to some gold and copper metallic fragments. Thus, by reacting **2** with 1 equiv of [AuCl(PPh$_3$)] in the presence of TlPF$_6$, the heterometallic Mn(I)/Au(I) complex **5** was obtained.[8] Similarly, the treatment of **2** with 0.5 equiv of [Cu(NCMe)$_4$]BF$_4$ (a source of Cu$^+$) gave the

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(4) Synthesis of **2**: To a solution of *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CH}] (0.30 g, 0.49 mmol) in CH$_2$Cl$_2$ (25 mL), (CN)$_2$ was bubbled through. The reaction was monitored by infrared spectroscopy, until all the starting material had been consumed (about 1 h). Bands corresponding to two new products, *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CH$_2$}]$^+$ and **2**, 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 **2** (0.11 g, 35% yield) as a white solid. Anal. Calcd for C$_{34}$H$_{29}$MnN$_2$O$_3$P$_2$: C, 64.77; H, 4.63; N, 4.44. Found: C, 64.73; H, 4.64; N, 4.13.

(5) Yuan-Fu, Yu; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1986**, *5*, 47.

(6) Selected spectroscopic data for **2** are as follows. IR (CH$_2$Cl$_2$, cm^{-1}): 2177 (w, ν(CN), CN^{t}Bu); 2143 (w, ν(CN)); 2023 (s), 1960 (m), 1945 (m) (ν(CO)). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 10.6 (br). ^{1}H NMR (CD$_2$Cl$_2$): δ 0.67 (s, CN^{t}Bu). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 17.7 (t, P$_2$C, ^1J(P–C) = 56 Hz).

(7) Selected spectroscopic data for **4-BF$_4$** are as follows. IR (CH$_2$Cl$_2$, cm^{-1}): 2240 (vw, ν(CN)); 2182 (m, ν(CN), CN^{t}Bu); 2052 (s), 1992 (s) (ν(CO)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 35.3 (br). ^{1}H NMR (CDCl$_3$): δ 6.20 (t, P$_2$CH, ^2J(PH) = 10 Hz), 0.88 (s, CN^{t}Bu).

(8) Synthesis of **5**: To a dichloromethane solution (15 mL) of *fac*-[Mn(CN^{t}Bu)(CO)$_3${(Ph$_2$P)$_2$CCN}] (0.1 g, 0.159 mmol), 79 mg of [AuCl(PPh$_3$)] (0.16 mmol) and 0.11 g of TlPF$_6$ (0.31 mmol) were added. The mixture was stirred at room temperature for 2 h. Then the white precipitate corresponding to TlCl was eliminated by filtration and the solution concentrated to ca. 5 mL. Slow diffusion of hexane into the mother liquor affords white crystals of **5** (0.16 g, 80% yield). Anal. Calcd for C$_{52}$H$_{44}$AuF$_6$MnN$_2$O$_3$P$_4$: C, 50.58; H, 3.59; N, 2.27. Found: C, 50.79; H, 3.51; N, 2.19.

trimetallic Mn(I)/Cu(I)/Mn(I) derivative **6**.[9] In both cases, coordination to the new metal through the nitrogen atom occurs. The analytical and spectroscopic data for **5** and **6** are in accordance with the structures proposed in Scheme 1.[10] Moreover, the structure of **6** was conclusively determined by X-ray crystallography.[11] The structure of the complex cation (Figure 2) contains two units of **2**, mutually rotated 108.6(5)°, bonded to the copper atom in a essentially linear coordination geometry ($N_3CuN_1 = 173.0(4)°$). Interestingly, **6** contains three metal atoms linked by two $[(PPh_2)_2CCN]^-$ groups. This anionic ligand is expected to have some charge delocalization along the P_2CCN skeleton,[12] and this may allow some degree of electronic interaction between the metals.

In conclusion, we describe in this work a general way to obtain the new coordinated ligand $[(PPh_2)_2CCN]^-$ by cleavage of cyanogen with bis(diphenylphosphino)methanide complexes, and we have shown its application for the synthesis of heterometallic species, by coordinating some additional metallic fragments through the free nitrogen atom of the cyano group.

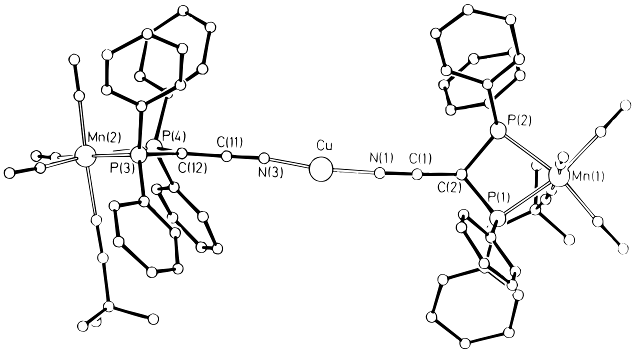

Figure 2. Crystal structure of complex **6**.

Acknowledgment. We thank the Spanish DGICYT (Project PB91-0678) for financial support.

Supporting Information Available: Text giving details of the X-ray study, tables of crystal data and refinement details, positional and thermal parameters, bond distances and angles, and torsion angles, and a fully labeled structure diagram for compound **6** (20 pages). Ordering information is given on any current masthead page.

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[9] Synthesis of **6**: To a solution of *fac*-$[Mn(CN^tBu)(CO)_3\{(Ph_2P)_2CCN\}]$ (0.1 g, 0.159 mmol) in CH_2Cl_2 (15 mL), 25 mg of $[Cu(NCMe)_4]BF_4$ (0.079 mmol) was added. The mixture was stirred at room temperature for 30 min. The volume of the solution was reduced to ca. 7 mL, and addition of hexane gave white crystals of **6** (0.19 g, 85%). Anal. Calcd for $C_{68}H_{58}BCuF_4Mn_2N_4O_6P_4$: C, 57.87; H, 4.14; N, 3.97. Found: C, 57.43; H, 4.22; N, 3.95.

[10] Selected spectroscopic data for **5** are as follows. IR (CH_2Cl_2, cm^{-1}): 2177 (m, ν(CN), CN^tBu); 2164 (m, ν(CN)); 2031 (s), 1964 (s), (ν(CO)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.0 (s, PPh_3), 16.0 (br, P_2C). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.8 (t, P_2C, $^1J(PC) = 49$ Hz). Selected spectroscopic data for **6** are as follows. IR (CH_2Cl_2, cm^{-1}): 2176 (m, ν(CN), CN^tBu); 2166 (m, ν(CN)); 2029 (s), 1964 (s), 1959 (s) (ν(CO)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 15.6 (br). ^1H NMR (CD_2Cl_2): δ 0.71 (s, CN^tBu). $^{31}C\{^1H\}$ NMR: δ 20.3 (t, P_2C, $^1J(PC) = 50$ Hz).

[11] Crystals of **6** lost solvent quickly, so the crystal used in this investigation was mounted for X-ray analysis directly from solution, and data were collected at −70 °C. In spite of this, unfortunately crystal decomposition occurred during data collection. Hence, although the identity of the complex was unambiguously established, the distances and angles may not be very reliable. Crystallographic details are given in the Supporting Information.

[12] Despite the above mentioned limitations of the crystallographic study,[11] it is interesting to note that the P−C(methanide) (average value 1.753(9) Å) and C(methanide)−CN (average value 1.382(14) Å) distances are slightly shorter than the value corresponding to a single bond, indicating contribution of both bond forms of Figure 1. As a consequence, the C≡N distances should be longer than that corresponding to a triple bond, but the effect of the contribution of form **b** is neutralized by the shortening that the CN bond of nitriles usually undergoes on coordination, resulting in a CN distance (average value 1.154(13) Å) of the same order as those found in free nitriles (1.16 Å in CH_3CN).