respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 26. All calculations were carried out on the Cray X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[27] The final atomic coordinates for the non-hydrogen atoms are given in Table V. The atomic coordinates of the hydrogen atoms are given in Table SI and thermal parameters in Tables SII and SIII (supplementary material).

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Registry No. **1a**, 133952-77-9; **1b**, 137966-74-6; **1c**, 137966-75-7; **1c**·CH_2Cl_2, 137966-76-8; **2**, 137966-78-0; **3**, 137966-80-4; **5**, 137966-82-6; **6**, 137966-84-8; $Pt_2Cl_2(\mu\text{-dppm})_2$, 61250-65-5; $Pt_2Br_2(\mu\text{-dppm})_2$, 61250-66-6; $Pt_2I_2(\mu\text{-dppm})_2$, 61289-07-4; $Pd_2Cl_2(\mu\text{-dppm})_2$, 64345-29-5; $[Pt_2(\mu\text{-I})_2(dppm)_2][BF_4]_2$, 132289-25-9; ^{195}Pt, 14191-88-9.

Supplementary Material Available: Hydrogen atom coordinates (Table SI) and anisotropic and isotropic thermal parameters for the non-hydrogen atoms (Tables SII and SIII) (3 pages); observed and calculated structure factors from the final cycle of least-squares refinement (Table SIV) (27 pages). Ordering information is given on any current masthead page.

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Reactions of Unsaturated Dihydrido Carbonyl Complexes of Manganese(I) with Nitriles and Isonitriles. Preparation and Characterization of the First Binuclear μ,η^1,η^2-NCR Derivatives

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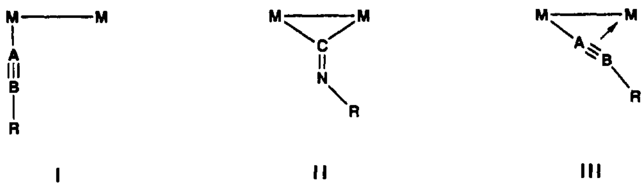
The unsaturated dihydrido binuclear carbonyl complexes $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-L-L})]$ (L-L = $Ph_2PCH_2PPh_2$, dppm (**1**), $(EtO)_2POP(OEt)_2$, tedip (**2**)) react under mild conditions with equimolecular amounts of nitriles NCR to give either $[Mn_2(\mu,\eta^1,\eta^2\text{-NCR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = Me (**3a**), Et (**3b**), Pr (**3c**), L-L = tedip, R = Me (**3d**), ^{t}Bu (**3e**)) or $[Mn_2(\mu\text{-H})(\mu\text{-N=CHR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = Ph (**4a**), CH_2Ph (**4b**), $CH{=}CH_2$ (**4c**), CH_2CN (**4d**); L-L = tedip, R = Ph (**4e**), $CH{=}CH_2$ (**4f**)) depending on the nature of the nitrile substituent. The compounds **3** are the first binuclear complexes containing a bridging σ,π-nitrile. At room temperature isocyanides replace both hydrido ligands in **1** and **2** to give $[Mn_2(\mu,\eta^1,\eta^2\text{-CNR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = ^{t}Bu (**5a**); L-L = tedip, R = ^{t}Bu (**5b**), 4-MeC_6H_4 (**5c**)) except in the case of *p*-tolyl isocyanide, which reacts with **1** to give $[Mn_2(\mu\text{-H})(\mu\text{-HC=N-4-MeC}_6H_4)(CO)_6(\mu\text{-dppm})]$ (**6**). The structures of **3a** and **4a** have been determined by X-ray diffraction methods. Crystals of **3a** are orthorhombic, space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions $a = 14.444$ (5), $b = 19.965$ (7), and $c = 11.207$ (5) Å. Crystals of **4a** are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 14.285$ (6), $b = 12.028$ (6), and $c = 10.902$ (6) Å and $\alpha = 86.74$ (3), $\beta = 105.32$ (2), and $\gamma = 97.59$ (2)°. Both structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1179 (**3a**) and 2118 (**4a**) observed reflections to R and R_w values of 0.0537 and 0.0693 (**3a**) and 0.0626 and 0.0738 (**4a**), respectively.

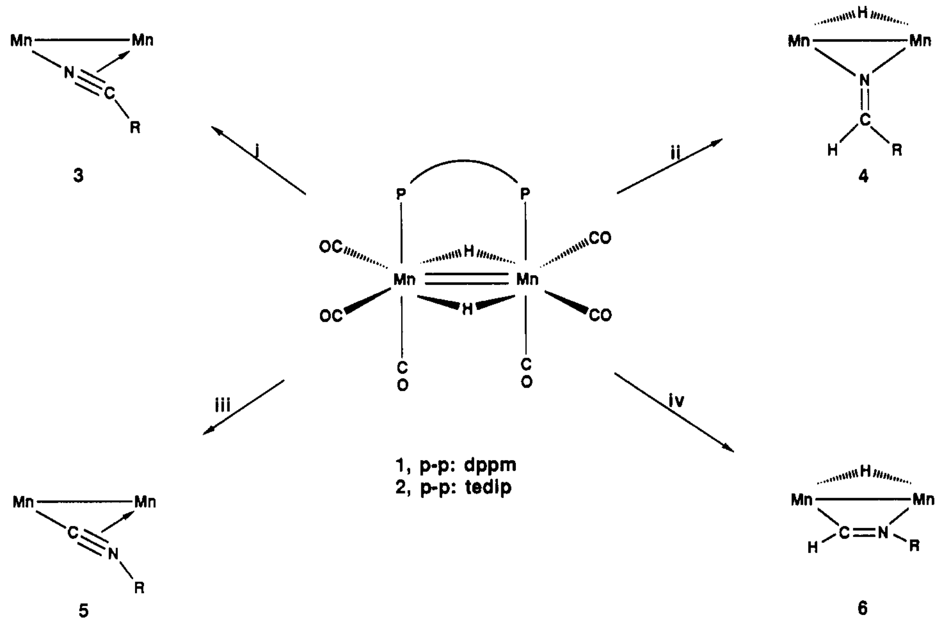
Introduction

There is much current interest in the interactions between small unsaturated molecules and metal clusters. In fact, the presence of several metal atoms allows for a great diversity of ligand coordination modes and promotes a wide variety of useful substrate transformations, some of which are appropriate models for reactions catalyzed by transition-metal surfaces. In this sense, much work has been devoted to the reactivity of carbon monoxide and hydrocarbyl ligands with metal clusters, while nitriles, NCR, and isonitriles, CNR, which are among the most versatile groups both in organic and organometallic chemistry,[1,2] have received less attention.

Chart I. Different Ways in Which Nitriles and Isonitriles Are Bonded to Two Metal Centers (ABR = CNR, NCR)



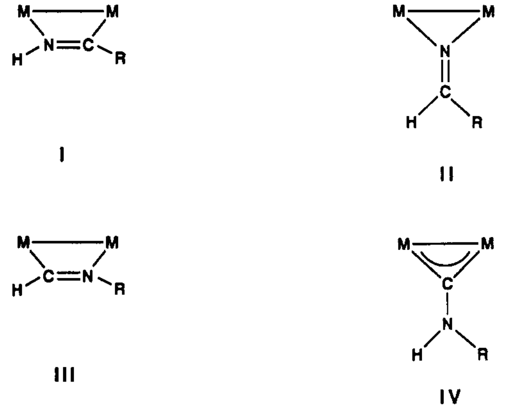
Scheme I. Reactions of Nitriles and Isonitriles with the Dimanganese Complexes 1 and 2 [Mn_2 = $(CO)_3Mn(\mu$-L-L$)Mn(CO)_3$, L-L = dppm, tedip]



Nitriles and isonitriles can interact with two metal centers in several different ways, as it is shown in Chart I, namely, as terminal σ-bonded, η^1-ABR (I)[2] (ABR = NCR, CNR), bridging σ-bonded, μ,η^1-CNR (II),[2] or bridging σ,-π-bonded, μ,η^1,η^2-ABR (III).[3,4]

The interaction of nitriles and isonitriles with metal complexes eventually leads to a partial (or total) hydrogenation of the substrates if the metal complex contains hydrido ligands or if the reaction is carried out in the presence of any other source of hydrogen, including molecular hydrogen. The reaction often stops at the first step, affording complexes in which a single hydrogen has been transferred to the nitrile or isonitrile ligand. The resulting new ligand can bridge two metal centers, as it is shown in Chart II. Thus, nitriles can originate NC-bonded μ-HN=CR μ-acimidoyl (I)[5] or μ-N=C(H)R μ-alkylidenimido (II)[5,6] ligands. On the other hand, isonitriles can give rise to μ-HC=NR N-substituted μ-formimidoyl (III)[7] or μ,η^1-C-N(H)R aminocarbyne ligands (IV).[4f,7a,8]

Chart II. Different Types of Ligands Bridging Two Metal Centers, Which Result after a Hydrogen Atom Has Been Transferred to a Nitrile or Isonitrile Ligand



Unsaturated dihydride species containing the moiety $M_2(\mu\text{-}H)_2$ (M=M formal double bond) usually react with nitriles and isonitriles giving any of the insertion products represented in Chart II.[4f,5,7] Sometimes it is also possible to detect[5c] or isolate[7a] simple addition products containing the fragment $(H)M(\mu\text{-}H)M(CNR)$ (M = Re, Os) as intermediate complexes in several of these insertion reactions. Finally, the reactions of complexes containing the moiety $M_2(\mu\text{-}H)_2$ (M=M formal double bond) may also lead to

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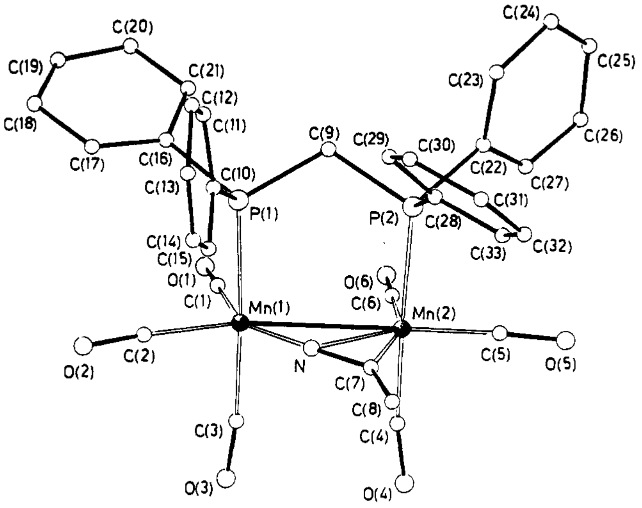

Figure 1. Molecular structure of $[Mn_2(\mu,\eta^1,\eta^2\text{-NCMe})(CO)_6(\mu\text{-dppm})]$ (**3a**) with the atom-numbering scheme.

bridging σ,π-isocyanide derivatives (III in Chart I).[4f]

Recently, we have prepared two new unsaturated dihydride species $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-dppm})]$ (1)[9] and $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-tedip})]$ (2).[10] We now report here the results of our studies on the reactivity of 1 and 2 toward nitriles and isonitriles, reactivity which differs markedly from that observed in related species. A preliminary account of this work has appeared previously.[9]

Results and Discussion

Reactions of 1 and 2 with Nitriles NCR. Nitriles NCR react under mild conditions with the dihydride complexes 1 and 2 either replacing both hydrido ligands or inserting into a manganese–hydrogen bond to give $[Mn_2(\mu,\eta^1,\eta^2\text{-NCR})(CO)_6(\mu\text{-L-L})]$ (3) or $[Mn_2(\mu\text{-H})(\mu\text{-N=CHR})(CO)_6(\mu\text{-L-L})]$ (4), respectively, depending on the nature of the nitrile substituent R (Scheme I).

Thus, alkanenitriles NCR containing electron-releasing groups R react slowly at room temperature, or faster at 60 °C, with equimolecular amounts of 1 and 2 to give $[Mn_2(\mu,\eta^1,\eta^2\text{-NCR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = Me (**3a**), Et (**3b**), Pr (**3c**); L-L = tedip, R = Me (**3d**), ${}^tBu$ (**3e**)) (i in Scheme I). The dihydride 1 fails to react with NC^tBu even at 60 °C, whereas some decomposition to *fac*-$[Mn(H)(CO)_3(dppm)]$ is observed in the reaction of 1 with butyronitrile at room temperature. No evidence of the formation of any intermediate complex is found by monitoring the reaction of 1 with NCMe by IR and NMR spectroscopies.

The structure of **3a** in solid state has been determined by X-ray diffraction methods, and it is shown in Figure 1. The spectroscopic data of complex **3a** are consistent with the solid-state structure. The most significant is the ${}^{13}C\{{}^1H\}$ NMR resonance at 157.2 ppm that can be assigned to the nitrile α-carbon, which is less shielded than a terminal nitrile α-carbon atom.[4h] The high asymmetry of the molecule is denoted by the nonequivalence of the six CO ligands that originate six ${}^{13}C\{{}^1H\}$ NMR resonances in the 240–210 ppm range and a very distorted pattern of ν_{CO} absorptions in the IR spectrum. In the ${}^{31}P\{{}^1H\}$ NMR spectrum one of the doublets of the AB system is broader than the other, due probably to the vicinity of a nitrogen atom of the bridging nitrile.

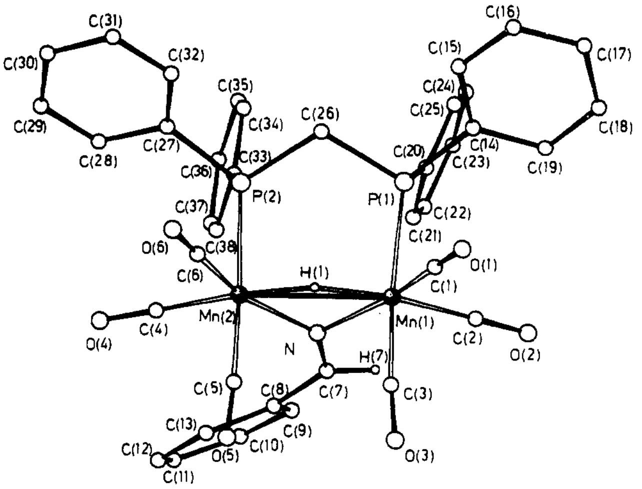

Figure 2. Molecular structure of $[Mn_2(\mu\text{-H})(\mu\text{-N=CHPh})(CO)_6(\mu\text{-dppm})]$ (**4a**) with the atom-numbering scheme.

All of the complexes **3b–e** have spectroscopic data very similar to those of **3a** (see Table I) and therefore should show similar structures. The ${}^{31}P\{{}^1H\}$ NMR resonances of **3d**,**e**, are very broad single peaks at room temperature, but at −60 °C the peak corresponding to **3e** is split into a AB system, being the half-height width temperature independent.

The formation of complexes 3 starting from unsaturated dihydride species is unprecedented. In fact the reaction of nitriles with complexes containing the moiety $M_2(\mu\text{-H})_2$ (M=M) leads usually to insertion derivatives[5,7] or, in the case of $[Os_3(\mu\text{-H})_2(CO)_{10}]$, to simple addition products[11] but not to complexes where the two hydride ligands have been substituted by a nitrile. Moreover, the obtention of the species $[Mn_2(\mu,\eta^1,\eta^2\text{-NCR})(CO)_6(\mu\text{-L-L})]$ is particularly noticeable, as σ,π-bonded nitrile complexes are scarce,[12] and to the best of our knowledge, complexes 3 are the first binuclear examples, although the synthesis of two fluxional dimolybdenum compounds, containing similar σ,π-cyanamide ligands $NCNR_2$ (R = H, Me), and the structure of one of them (R = Me) have been reported.[3]

On the other hand, the reaction of nitriles NCR containing electron-withdrawing substituents R with equimolecular amounts of 1 and 2 at room temperature yields the insertion products $[Mn_2(\mu\text{-H})(\mu\text{-N=CHR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = Ph (**4a**), CH_2Ph (**4b**), $CH{=}CH_2$ (**4c**), CH_2CN (**4d**); L-L = tedip, R = Ph (**4e**), $CH{=}CH_2$ (**4f**) (ii in Scheme I)).

The structure of complexes 4 is supported by the spectroscopic data collected in Table I and by the X-ray crystal structure of **4a**, shown in Figure 2. The ${}^{13}C\{{}^1H\}$ NMR resonance for the carbon atom of the alkylidenimido group N=CHR is located at 177–160 ppm, while the proton signal of the same group is observed at 9–10 ppm. The three ${}^{13}C\{{}^1H\}$ NMR resonances in the 230–210 ppm region that are assigned to the terminal carbonyl ligands and the pattern of the ν_{CO} absorptions in the infrared spectrum point out that the CO ligands are insensitive to the asymmetry introduced in the molecule by the alkylidenimido group. All these complexes exhibit a single peak in their ${}^{31}P\{{}^1H\}$ NMR spectra at room temperature, except

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Table I. Spectroscopic Data for the New Compounds

compd	ν_{CO}[a]	^{1}H NMR[b]	^{13}C{^{1}H} NMR[b]	^{31}P{^{1}H} NMR[b]
[Mn$_2$(μ,η^1,η^2-N≡CMe)-(CO)$_6$(μ-dppm)] (**3a**)	2025 vs, 1970 vs, 1945 s, 1910 s, 1890 m	7.4 (m, 4 Ph); 3.2 (m), 2.42 (m) (P–CH$_2$–P); 2.2 (s, CH$_3$)	231.5 (d, J_{PC} = 24, CO); 230.6 (d, J_{PC} = 27, CO); 227.1 (d, J_{PC} = 22, CO); 222.7 (d, J_{PC} = 24, CO); 216.4 (d, J_{PC} = 27, CO); 214.7 (d, J_{PC} = 39, CO); 157.2 (m, N≡C); 137–128 (m, 4 Ph); 38.2 (m, P–CH$_2$–P); 15.6 (s, CH$_3$)	56.2, 54.2 (AB syst, J_{AB} = 65)
[Mn$_2$(μ,η^1,η^2-N≡CEt)-(CO)$_6$(μ-dppm)] (**3b**)	2030 vs, 1970 vs, 1952 s, 1910 vs, 1890 m	7.9–6.6 (m, 4 Ph); 3.2 (m), 2.5 (m) (P–CH$_2$–P); 2.3 (m, CH$_3$–CH$_2$); 1.17 (t, CH$_3$–CH$_2$, J_{PH} = 12)	231.9 (br, CO); 231.3 (br, CO); 227.5 (br, CO); 223.6 (br, CO); 217.1 (br, CO); 215.7 (d, J_{PC} = 38, CO); 164.9 (m, N≡C); 135–125 (m, 4 Ph); 38.2 (m, P–CH$_2$–P); 24.6 (s, CH$_3$–CH$_2$); 12.2 (s, CH$_3$–CH$_2$)	57.1, 54.1 (AB syst, J_{AB} = 65)
[Mn$_2$(μ,η^1,η^2-N≡CPr)-(CO)$_6$(μ-dppm) (**3c**)	2021 s, 1968 s, 1948 s, 1909 s, 1886 m,	7.9–6.6 (m, 4 Ph); 3.2 (m, P–CH$_2$–P); 2.4 (m, –CH$_2$–CN); 1.8 (m, CH$_3$–CH$_2$–); 0.9 (br, CH$_3$)	228.3 (br, CO); 227.1 (br, CO); 225.6 (br, CO); 223.4 (br, CO); 220.7 (br, CO); 218.3 (br, CO); 163.2 (m, N≡C); 136–127 (m, 4 Ph); 38.6 (t, J_{PC} = 8, P–CH$_2$–P); 32.8 (s, –CH$_2$–CN); 22.2 (s, CH$_3$–CH$_2$–); 14.0 (s, CH$_3$)	57.3, 54.4 (AB syst, J_{AB} = 65)
[Mn$_2$(μ,η^1,η^2-N≡CMe)-(CO)$_6$(μ-tedip)] (**3d**)	2040 s, 1985 vs, 1960 s, 1927 vs, 1908 sh	4.0 (m, 2 –CH$_2$–); 3.9 (m, –CH$_2$–); 3.7 (m, –CH$_2$–); 2.8 (s, NC–CH$_3$); 1.3 (t, J_{HH} = 6, 2 –CH$_2$–CH$_3$); 1.2 (t, J_{HH} = 6, 2 –CH$_2$–CH$_3$)	228.6 (br, 2 CO); 226.3 (br, CO); 222.0 (br, CO); 213.6 (br, CO); 209.4 (br, CO); 155.8 (m, N≡C); 62.0 (s, –CH$_2$–); 61.8 (s, 2 –CH$_2$–); 61.0 (s, –CH$_2$–); 16.4 (s, NC–CH$_3$); 16.1 (s, 2 CH$_2$–CH$_3$); 15.9 (s, 2 CH$_2$–CH$_3$);	167.8
[Mn$_2$(μ,η^1,η^2-N≡C^{t}Bu)-(CO)$_6$(μ-tedip) (**3e**)	2035 s, 1983 vs, 1966 s, 1926 vs, 1905 m	4.0 (m, 2 –CH$_2$–); 3.8 (m, –CH$_2$–); 3.7 (m, –CH$_2$–); 1.4 (s, NC–C(CH$_3$)$_3$); 1.2 (br, 3 –CH$_2$–CH$_3$); 1.1 (br, –CH$_2$–CH$_3$)	229.2 (br, CO); 228.5 (br, CO); 225.7 (br, CO); 222.1 (br, CO); 216.3 (br, CO); 213.8 (d, J_{PC} = 58, CO); 168.1 (m, N≡C); 61.9 (s, –CH$_2$–); 61.8 (s, 2 –CH$_2$–); 61.0 (s, –CH$_2$–); 38.2 (s, NC–C(CH$_3$)$_3$); 29.2 (s, NC–C(CH$_3$)$_3$); 16.0 (s, 2 CH$_2$–CH$_3$); 15.9 (s, 2 CH$_2$–CH$_3$);	167.8; 167.9, 166.7[c] (AB syst, J_{AB} = 64)
[Mn$_2$(μ-H)(μ-N═CHPh)-(CO)$_6$(μ-dppm)] (**4a**)	2030 vs, 2000 vs, 1948 s, 1930 sh, 1910 vs	10.2 (s, N═CH); 7.7–6.7 (m, 5 Ph); 2.6 (m, CH$_2$); –11.9 (t, J_{PH} = 20; Mn–H–Mn)	222.7 (br, 2 CO); 219.3 (br, 2 CO); 215.0 (br, 2 CO); 177.1 (s, N═CH); 140.8 (s, C$_1$–N═CH); 132.5–126.6 (m, 5 Ph); 24.6 (t, J_{PC} = 16, P–CH$_2$–P)	51.7 s; 51.3, 49.7[d] (AB syst, J_{AB} = 99)
[Mn$_2$(μ-H)(μ-N═CH-CH$_2$Ph)-(CO)$_6$(μ-dppm)] (**4b**)	2030 vs, 1997 vs, 1942 m, 1925 sh, 1915 vs	9.0, 4.0, 3.9 (ABX syst, (J_{AB} = 15, J_{BX} = J_{AX} = 5, N═CH–CH$_2$–Ph); 7.5–7.0 (m, 5 Ph); 2.3 (t, J_{PH} = 11, P–CH$_2$–P); –12.2 (t, J_{PH} = 21, Mn–H–Mn)	223.2 (br, 2 CO); 220.5 (br, 2 CO); 218.3 (br, 2 CO); 178.3 (s, N═CH); 133.3–126.7 (m, 5 Ph); 50.9 (s, CH$_2$–Ph); 20.2 (t, J_{PC} = 12, P–CH$_2$–P)	52.2, 49.1 (AB syst, J_{AB} = 103)
[Mn$_2$(μ-H)(μ-N═CHCH═CH$_2$)-(CO)$_6$(μ-dppm)] (**4c**)	2030 s, 2000 s, 1950 m, 1925 sh, 1912 vs	9.5 (s, N═CH); 7.4–7.2 (m, 4 Ph); 6.9 (m, HC═CH$_2$); 5.7 (d, $^3J_{HH}$ = 9, HC═CH$_{cis}$H); 5.6 (d, $^3J_{HH}$ = 27, HC═CH$_{trans}$H); 2.4 (m, P–CH$_2$–P); –12.1 (t, J_{PH} = 20, Mn–H–Mn)	223.1 (br, 2 CO); 220.3 (br, 2 CO); 214.8 (br, 2 CO); 178.5 (s, N═CH); 140.1 (s, HC═CH$_2$); 134.7–128.3 (m, 4 Ph); 123.3 (s, HC═CH$_2$); 21.5 (m, P–CH$_2$–P)	51.0; 49.8, 48.5[e] (AB syst, J_{AB} = 159)
[Mn$_2$(μ-H)(μ-N═CHCH$_2$CN)-(CO)$_6$(μ-dppm)] (**4d**)	2030 s, 2000 s, 1950 m, 1925 sh, 1916 vs	8.8 (s, N═CH); 7.5–7.1 (m, 4 Ph); 3.5 (m, –CH$_2$–C≡N); 2.4 (m), 2.3 (m) (P–CH$_2$–P); –12.4 (t, J_{PH} = 21, Mn–H–Mn)	222.9 (br, 2 CO); 219.2 (d, J_{PC} = 59, 2 CO); 214.1 (d, J_{PC} = 53, 2 CO); 163.6 (s, N═CH); 135.8–128.5 (m, 4 Ph); 116.1 (s, CH$_2$–C≡N); 30.5 (s, CH$_2$–C≡N); 19.4 (t, J_{PC} = 23, P–CH$_2$–P)	50.9
[Mn$_2$(μ-H)(μ-N═CHPh)-(CO)$_6$(μ-tedip)] (**4e**)	2040 s, 2012 s, 1987 m, 1960 s, 1920 vs	9.9 (s, N═CH); 7.5–7.2 (m, 1 Ph); 4.0 (m, 3 –CH$_2$–); 3.5 (m, –CH$_2$–); 1.3 (br, 3 –CH$_2$–CH$_3$); 1.0 (br, –CH$_2$–CH$_3$); –13.1 (t, J_{PH} = 28, Mn–H–Mn)	220.4 (br, 2 CO); 216.9 (br, 2CO); 212.7 (br, 2CO); 177.3 (s, N═CH); 104.1, 127.9, 127.1, 125.9 (1:2:2:1, C$_6$H$_5$); 61.0 (s, –CH$_2$–); 60.5 (s, 2 –CH$_2$–); 60.1 (s, –CH$_2$–); 15.1 (s, CH$_2$–CH$_3$); 14.9 (s, 2 CH$_2$–CH$_3$); 14.6 (s, CH$_2$–CH$_3$)	166.3
[Mn$_2$(μ-H)(μ-N═CHCH═CH$_2$)-(CO)$_6$(μ-tedip)] (**4f**)	2040 vs, 2009 s, 1987 m, 1964 s, 1925 vs	9.2 (s, N═CH); 7.2 (br, HC═CH$_2$); 6.6 (d, $^3J_{HH}$ = 14, HC═CH$_{cis}$H); 5.5 (d, $^3J_{HH}$ = 17, HC═CH$_{trans}$H); 4.1 (m, 2 –CH$_2$–); 3.9 (m, –CH$_2$–); 3.8 (m, –CH$_2$–); 1.3 (br, 3 –CH$_2$–CH$_3$); 1.1 (br, –CH$_2$–CH$_3$); –13.2 (t, J_{PH} = 26, Mn–H–Mn)	222.0 (br, 2 CO); 218.7 (br, 2 CO); 212.9 (br, 2 CO) 178.9 (s, N═CH); 140.1 (s, HC═CH$_2$); 122.8 (s, HC═CH$_2$); 61.6 (m, –CH$_2$–); 15.9 (s, –CH$_3$)	166.4
[Mn$_2$(μ,η^1,η^2-C≡N^{t}Bu)-(CO)$_6$(μ-dppm)] (**5a**)	2030 vs,[f] 1975 vs, 1952 s, 1912 s, 1890 m	8.0–6.8 (m, 4 Ph); 3.4 (m), 2.5 (m) (–CH$_2$–); 1.0 (s, C–(CH$_3$)$_3$)	232.0 (br), 227.5 (br), 226.4 (br), 224.3 (br), 223.0 (m) (1:2:2:1:1, 6 CO, C≡N–); 135.4–127.9 (m, 4 Ph); 60.3 (s, C–(CH$_3$)$_3$); 42.0 (t, J_{PC} = 12, –CH$_2$–); 30.8 (s, C–(CH$_3$)$_3$)	68.6, 60.4 (AB syst, J_{AB} = 80)

Table I (Continued)

compd	ν_{CO}[a]	^1H NMR[b]	$^{13}C\{^1H\}$ NMR[b]	$^{31}P\{^1H\}$ NMR[b]
[$Mn_2(\mu,\eta^1,\eta^2$-C≡N^{t}Bu)-$(CO)_6(\mu$-tedip)] (**5b**)	2036 vs,[f] 1987 vs, 1963 s, 1928 s, 1906 m	4.0 (m, 2 $-CH_2-$); 3.9 (m, 2 $-CH_2-$); 1.4 (br, 2 $-CH_2-CH_3$); 1.3 (br, 2 $-CH_2-CH_3$); 1.1 (s, C$-(CH_3)_3$)	226.7 (br), 223.5 (br), 221.3 (br), 213.0 (br), 202.0 (m) (1:2:2:1:1, 6 CO, C≡N–); 61.0 (s, $-CH_2-$); 60.9 (s, $-CH_2-$); 60.2 (s, $-CH_2-$); 60.1 (s, $-CH_2-$); 58.8 (s, $C(CH_3)_3$); 29.9 (s, $C(CH_3)_3$); 15.1 (s, 2 CH_2-CH_3); 15.0 (s, 2 CH_2-CH_3)	179.8 (br), 164.6 (br) (AB syst); 178.8, 164.1[g] (AB syst, J_{AB} = 81)
[$Mn_2(\mu,\eta^1,\eta^2$-C≡N-2,6-C_6H_3-$(CH_3)_2)(CO)_6(\mu$-tedip)] (**5c**)	2040 s,[f] 1999 s, 1971 s, 1933 s, 1912 m	7.4, 7.2 (AX syst, J_{AX} = 8, C_6H_4); 4.2 (m, 3 CH_2); 3.6 (m, CH_2); 2.4 (s, $C_6H_4-CH_3$); 1.4 (t, $^3J_{HH}$ = 7, CH_2-CH_3); 1.3 (t, $^3J_{HH}$ = 7, CH_2-CH_3); 1.2 (t, $^3J_{HH}$ = 7, CH_2-CH_3); 0.9 (t, $^3J_{HH}$ = 7, CH_2-CH_3)	235.8 (d, J_{PC} = 38), 227.2 (d, J_{PC} = 36); 224.2 (d, J_{PC} = 30), 221.5 (t, J_{PC} = 30); 215.4 (d, J_{PC} = 41), 212.6 (d, J_{PC} = 61); (1:1:1:2:1:1, 6 CO, C≡N–); 136.6 s, 129.8 s, 123.8, 121.0 s (1:2:2:1, C_6H_5); 62.1 (m, CH_2); 20.9 (s, $C_6H_4-CH_3$); 15.8 (m, CH_2-CH_3)	177.4, 163.3 (AB syst, J_{AB} = 74)
[$Mn_2(\mu$-H)(μ-CH=N-4-C_6H_4Me)$(CO)_6(\mu$-dppm)] (**6**)	2040 s, 2010 s, 1955 s, 1935 m, 1920 s	10.9 (s, N=CH); 7.8–7.2 (m, 5 Ph); 3.1 (m, $-CH_2-$); 1.4 (s, $-CH_3$); −18.0 (t, J_{PH} = 25, Mn–H–Mn)	241.2 (d, J_{PC} = 28, N=CH); 222.0 (d, J_{PC} = 24, 2 CO); 221.0 (d, J_{PC} = 14, 2 CO); 218.9 (d, J_{PC} = 14, 2 CO); 157.3 (s, C_1 –N=CH); 136.6–123.5 (m, 5 Ph); 25.9 (t, J_{PC} = 14, $-CH_2-$); 20.8 (s, $-CH_3$)	53.7, 49.5 (AB syst, J_{AB} = 49)

[a] In toluene unless otherwise stated. In cm^{-1}. [b] In $CDCl_3$, at room temperature, unless otherwise noted. δ in ppm, J in Hz. [c] CD_2Cl_2/CH_2Cl_2, −60 °C. [d] $CDCl_3$, −30 °C. [e] CD_2Cl_2/CH_2Cl_2, −93 °C. [f] ν_{CN}(Nujol): 1768 m (**5a**), 1785 m (**5b**), 1733 (**5c**). [g] CD_2Cl_2/CH_2Cl_2, −50 °C.

4b, which presents an AB system. However, the solid-state structure of **4a** and the AB patterns observed for complexes **4a** and **4c** at lower temperatures (−30 and −93 °C, respectively) suggest that complexes **4**, with the single exception of **4b**, are fluxional.

Although similar dynamic processes have not been reported for binuclear complexes having a bridging alkylidenimido ligand, not even for [$Re_2(\mu$-H)(μ-N=CHMe)-$(CO)_6(\mu$-L-L)] (L-L = dppm, tedip),[5c] a tautomerization of terminal alkylidenimido ligands in a mononuclear zirconium compound has been described.[13]

The mild conditions under which complexes **3** and **4** were obtained contrast with the more forcing conditions required by [$Re_2(\mu$-H$)_2(CO)_6(\mu$-L-L)] (L-L = dppm, tedip),[5c] which do not react with NCMe but in refluxing acetonitrile. The moderate conditions the complexes **1** and **2** require to react with nitriles are probably due to the weakness of the manganese–hydrogen bond in comparison with the rhenium–hydrogen bond.

Reactions of 1 and 2 with Isonitriles CNR. Excepting for the case of the reaction of **1** with *p*-tolyl isocyanide, which leads to the formation of a formimidoyl derivative [$Mn_2(\mu$-H)(μ-4-MeC_6H_4N=CH)$(CO)_6(\mu$-dppm)] (**6**) (iv in Scheme I), the complexes **1** and **2** react instantaneously with equimolecular amounts of isocyanides CNR to give [$Mn_2(\mu$-η^1,η^2-CNR)$(CO)_6(\mu$-L-L)] (L-L = dppm, R = ^{t}Bu (**5a**); L-L = tedip, R = ^{t}Bu (**5b**), 4-MeC_6H_4 (**5c**)) (iii in Scheme I). The reaction of **2** with CN-4-MeC_6H_4 gives actually a mixture of complexes, from which the main product, **5c**, could not be completely separated. Further purification of **5c** was not possible, and therefore, it could be only spectroscopically characterized.

The spectroscopic data of complexes **5**, collected in Table I, support the proposed structure for these compounds. Thus, they present an IR band of medium intensity at about 1760 cm^{-1}, which should correspond to the σ,π-bonded isocyanide ligands as well as five ν_{CO} absorptions in the 2100–1880 cm^{-1} range with a pattern very similar to that observed for complexes **3**. On the other hand, their $^{13}C\{^1H\}$ NMR spectra show five signals with a 1:2:2:1:1 intensity ratio in the 250–200 ppm range, assigned to six carbonyl carbon nuclei and to the isocyanide α-carbon atom. The existence of five different CO $^{13}C\{^1H\}$ NMR resonances corroborates the low symmetry of the molecular structure.

The presence of a three-electron-donor, bridging formimidoyl group (HC=N-4-MeC_6H_4) in complex **6** is mainly supported by its $^{13}C\{^1H\}$ NMR resonance at 241.2 ppm, corresponding to a C atom attached to a H nucleus, and the ^1H NMR signal at 10.9 ppm (see Table I). Accordingly its $^{31}P\{^1H\}$ NMR spectrum exhibits an AB pattern, but the pattern of the ν_{CO} infrared absorptions as well as the three CO $^{13}C\{^1H\}$ NMR resonances does not reflect the lack of a symmetry plane in the molecule.

In the reactions of isocyanides with **1** and **2** it is not clear why the products are most often σ,π-bridging isocyanide derivatives while **1** reacts with CN-4-MeC_6H_4 to give the insertion compound **6**. Usually unsaturated dihydrides react with isocyanides to give insertion products,[5c,7,4f] although there are examples in which the product is a simple addition derivative[7a] or even a σ,π-bridging isocyanide compound.[4f] However, only [$W_2(\mu$-H$)_2(CO)_4(\eta^5$-$C_5H_5)_2$] like **1** gives either insertion products or σ,π-bridging isocyanide derivatives depending on the nature of the isocyanide substituent.[4f]

The first step of the reactions of **1** and **2** with nitriles and isonitriles should begin very similarly with the formation of the simple addition products [(H)$(CO)_3$Mn(μ-H)(μ-L-L)Mn$(CO)_3$(ABR)] (ABR = NCR, CNR) (**7**). The coordinated nitriles or isocyanides could subsequently replace both hydride ligands or insert into the manganese–hydrogen bond to afford the observed products.

Although there is not any experimental evidence for the formation of complexes **7**, it is reasonable to assume their existence as intermediate compounds. Complexes of similar composition have been detected or obtained in the reactions of unsaturated dihydrides with nitriles, isonitriles, or phosphines.[5c,7a,9]

Description of the Structures of Compounds 3a and 4a. The structures of **3a** and **4a** are shown in Figure 1 and 2 respectively, together with the atom-numbering systems. A summary of the important bond distances and angles is given in Table II. The substitution of two hydrides in **1** by the four-electron-donor N≡CMe ligand, σ,π-interacting, results in the elongation of the unsaturated Mn–Mn bond from 2.699 (2) to 2.865 (4) Å, this latter value being comparable to that found in the structure of $Mn_2(CO)_{10}$

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(13) Erker, G.; Frömberg, W.; Krüger, C. K.; Raabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400.

Table II. Important Interatomic Distances (Å) and Angles (deg) for Compounds 3a and 4a

	Compound **3a**		
Mn(1)–Mn(2)	2.865 (4)	Mn(2)–C(4)	1.79 (2)
Mn(1)–P(1)	2.323 (6)	Mn(2)–C(5)	1.75 (2)
Mn(1)–C(1)	1.79 (2)	Mn(2)–C(6)	1.79 (3)
Mn(1)–C(2)	1.80 (2)	Mn(2)–N	2.10 (1)
Mn(1)–C(3)	1.86 (2)	Mn(2)–C(7)	2.10 (2)
Mn(1)–N	1.88 (2)	N–C(7)	1.25 (3)
Mn(2)–P(2)	2.334 (6)	C(7)–C(8)	1.48 (3)
P(1)–Mn(1)–Mn(2)	92.7 (2)	N–Mn(1)–C(3)	92.5 (8)
C(1)–Mn(1)–Mn(2)	103.7 (8)	P(2)–Mn(2)–Mn(1)	92.9 (2)
C(3)–Mn(1)–Mn(2)	90.1 (7)	C(4)–Mn(2)–Mn(1)	89.5 (7)
N–Mn(1)–Mn(2)	47.3 (5)	C(6)–Mn(2)–Mn(1)	83.6 (8)
C(1)–Mn(1)–P(1)	87.5 (7)	C(5)–Mn(2)–P(2)	87.2 (8)
C(2)–Mn(1)–P(1)	89.7 (7)	C(6)–Mn(2)–P(2)	92.0 (8)
N–Mn(1)–P(1)	89.6 (5)	C(5)–Mn(2)–C(4)	90.4 (11)
C(2)–Mn(1)–C(1)	96.3 (10)	C(6)–Mn(2)–C(4)	89.3 (11)
C(3)–Mn(1)–C(1)	91.6 (10)	C(6)–Mn(2)–C(5)	98.0 (11)
C(3)–Mn(1)–C(2)	87.7 (10)	Mn(1)–N–C(7)	163 (1)
N–Mn(1)–C(2)	112.9 (9)	N–C(7)–C(8)	137 (2)
	Compound **4a**		
Mn(1)–Mn(2)	2.818 (4)	Mn(2)–C(4)	1.76 (2)
Mn(1)–P(1)	2.350 (5)	Mn(2)–C(5)	1.81 (2)
Mn(1)–C(1)	1.79 (2)	Mn(2)–C(6)	1.81 (2)
Mn(1)–C(2)	1.80 (2)	Mn(2)–N	1.998 (10)
Mn(1)–C(3)	1.80 (2)	N–C(7)	1.28 (2)
Mn(1)–N	2.011 (13)	C(7)–C(8)	1.46 (3)
Mn(2)–P(2)	2.339 (5)		
P(1)–Mn(1)–Mn(2)	93.2 (2)	C(6)–Mn(2)–Mn(1)	113.8 (6)
C(1)–Mn(1)–Mn(2)	117.9 (5)	N–Mn(2)–Mn(1)	45.1 (3)
C(3)–Mn(1)–Mn(2)	91.5 (6)	C(4)–Mn(2)–P(2)	87.4 (6)
N–Mn(1)–Mn(2)	45.1 (3)	C(6)–Mn(2)–P(2)	87.8 (6)
C(1)–Mn(1)–P(1)	89.2 (5)	N–Mn(2)–P(2)	94.2 (3)
C(2)–Mn(1)–P(1)	88.1 (5)	C(5)–Mn(2)–C(4)	89.8 (8)
N–Mn(1)–P(1)	97.4 (4)	C(6)–Mn(2)–C(4)	93.6 (9)
C(2)–Mn(1)–C(1)	94.6 (8)	N–Mn(2)–C(4)	107.1 (7)
C(3)–Mn(1)–C(1)	87.7 (7)	C(6)–Mn(2)–C(5)	91.3 (8)
C(3)–Mn(1)–C(2)	88.5 (8)	N–Mn(2)–C(5)	87.5 (6)
N–Mn(1)–C(2)	102.5 (6)	Mn(1)–N–Mn(2)	89.3 (5)
N–Mn(1)–C(3)	86.6 (7)	C(7)–N–Mn(1)	128.1 (12)
P(2)–Mn(2)–Mn(1)	91.9 (2)	C(7)–N–Mn(2)	142.2 (12)
C(5)–Mn(2)–Mn(1)	91.1 (5)	N(1)–C(7)–C(8)	129.7 (18)

[2.904 (1) Å],[14] in which a single metal–metal bond must be envisaged. The nitrile group is σ-bonded to the Mn(1) atom [Mn(1)–N = 1.88 (2) Å] in a slightly bent manner, as shown by the Mn(1)–N–C(7) angle, 163 (1)°. The π interaction between the N–C(7) triple bond and the Mn(2) atom is symmetrical, the Mn(2)–N and Mn(2)–C(7) lengths being of 2.10 (1) and 2.10 (2) Å, respectively. The value of the N–C(7) bond distance, 1.25 (3) Å, corresponds to that expected for a double bond. The dppm bridge has an "envelope" conformation with Mn(1), Mn(2), P(1), and P(2) atoms coplanar. Also the Mn(1), Mn(2), N, and C(7) atoms are also nearly coplanar, the two bridges being practically perpendicular to one another [the dihedral angle between them is 91.5 (4)°].

In $[Mo_2(\mu,\eta^1,\eta^2\text{-}NCNMe_2)(\eta^5\text{-}C_5H_5)_2(CO)_4]$, the (dimethylamino)cyanamide ligand behaves in a similar way to the nitrile in **3a**, σ,π-interacting with two Mo atoms at a distance of 3.056 (1) Å, even if the nitrogen atom of the amine substituent imparts peculiar properties to the ligand. In fact from the structural results the resonance form $:\ddot{N}^-{=}C{=}N^+R_2$ seems to be enhanced with respect to the one $:N{\equiv}C{-}NR_2$. The value of the Mo(1)–N σ-bond distance is 2.056 (6) Å, and those of the Mo(2)–N and Mo(2)–C π-bond distances are 2.149 (5) and 2.103 (7) Å, while the Mo(1)–N–C angle is markedly bent, 134.6 (5)°.[3]

It can be interesting to compare the structural parameters of **3a** with those found in $[Mn_2(\mu,\eta^1,\eta^2\text{-}CN\text{-}4\text{-}MeC_6H_4)(CO)_4(\mu\text{-dppm})_2$ in which an isocyanide ligand σ,π-interacts with two Mn atoms. The Mn–Mn separation is slightly longer, 2.936 (2) Å, the Mn(1)–C σ-bond is 1.81 (1) Å, the Mn(2)–C and Mn(2)–N π-bond distances are 2.14 (1) and 2.12 (1) Å, and the Mn(1)-C-N and C-N-C angles are 168.1 (9) and 137.2 (9).[4a]

In **4a** the nitrile N≡CPh inserts into one of the Mn–H bonds of **1** with shift of the hydride on the carbon atom and formation of the 3-electron-donor μ-N=C(H)Ph bridging alkylidenimido ligand. The Mn–Mn separation is now of 2.818 (4) Å, shorter than that found in **3a**. The bonding of the N atom to the two metals is symmetrical, the Mn(1)–N and Mn(2)–N bond distances being of 2.011 (13) and 1.998 (10) Å, respectively. The hydride bridge is almost coplanar with the alkylidenimido bridge. The dppm bridge has an "envelope" conformation with Mn(1), Mn(2), P(1), and P(2) atoms coplanar and is almost perpendicular to the other two bridges.

In the $[Mn_2\{\mu\text{-}N{=}C(CF_3)_2)\}_2(CO)_7]$, where the two Mn atoms are triply bridged by two alkylidenimido and one carbonyl ligands, a rather short Mn–Mn separation, 2.518 (1) Å, has been found, while the Mn–N, 2.021 (7), 1.999 (7), 2.036 (7), and 1.972 (7) Å, and the N–C, 1.259 (9) and 1.258 (9) Å, bond distances are comparable to those of **4a**.[6a]

Experimental Section

All reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents used were dried and distilled under nitrogen. The petroleum ether used was the fraction with boiling point 62–66 °C. Nitriles and isonitriles were purchased from Aldrich and used as received except *p*-tolyl isocyanide, which was prepared according to a literature procedure.[15] Alumina for column chromatography was deactivated by appropriate addition under nitrogen of deoxygenated water to the commercial material (Aldrich, neutral, activity 1). Infrared spectra were recorded on a Perkin-Elmer 1720-Y infrared Fourier transform spectrometer. Proton, carbon, and phosphorus magnetic resonances spectra (NMR) were measured on a Bruker AC-300 instrument at 300.13, 75.47, and 121.49 MHz, respectively. Chemical shifts are referred to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4. ^{13}C NMR assignments were routinely supported on standard DEPT[16] experiments. Elemental C, H, and N analyses were obtained with a Perkin-Elmer 240 B microanalizer.

Preparation of $[Mn_2(\mu,\eta^1,\eta^2\text{-}NCMe)(CO)_6(\mu\text{-dppm})]$ (3a). MeCN (8 mL, 0.153 mmol) was added to a solution of **1**·toluene (0.1 g, 0.133 mmol) in toluene (20 mL). The resulting mixture was heated 1.5 h at 60 °C until the starting material was consumed, as evidenced the IR spectrum of the mixture and the color change of the solution from red violet to orange. Solvent was then removed under vacuum, and the residue was dissolved in toluene and filtered through Celite. Crystallization from toluene/petroleum ether at −20 °C afforded orange crystals of **3a** (66%). Anal. Calc for $C_{33}H_{25}NO_6P_2Mn_2$ (**3a**): C, 56.35; H, 3.58; N, 1.99. Found: C, 56.59; H, 3.54; N, 2.00.

Preparation of $[Mn_2(\mu,\eta^1,\eta^2\text{-}NCPr)(CO)_6(\mu\text{-dppm})]$ (3c). A mixture of **1**·toluene (0.1 g, 0.133 mmol) and butyronitrile (14 μL, 0.16 mmol) in toluene (20 mL) was stirred for 4 days at room temperature. After removal of the solvent under reduced pressure, the residue was chromatographied on an alumina column (activity IV, 14 × 2.5 cm). Two major yellow bands were collected, the first containing *fac*-[Mn(H)(CO)$_3$(dppm)] was eluted with petroleum ether. The second, eluted with toluene/petroleum ether (1/3), afforded complex **3c**, which was recrystallized from tolu-

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[14] Churchill, M. R.; Amoh, K. N.; Wassermann, H. J. *Inorg. Chem.* **1981**, *20*, 1609 (structure determined at room temperature). In the structure determined at low temperature (74 K) the Mn–Mn distance was found to be 2.895 (1) Å (Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr., Sect. B* **1982**, *38*, 6).

[15] Weber, W. P.; Gokel, G. W.; Ugi, I. *Angew. Chem.* **1972**, *84*, 587.

[16] Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy. A guide for chemists*; Oxford University Press: Oxford, England, 1987; pp 253–256.

ene/petroleum ether to yield orange-red crystals (58%). Anal. Calc for $C_{35}H_{29}NO_6P_2Mn_2$ (**3c**): C, 57.48; H, 3.99; N, 1.92. Found: C, 57.31; H, 4.02; N, 1.90.

Preparation of Complexes 3b,d,e and 4a–f. All these complexes were prepared following the same general procedure. A solution of **1**·toluene or **2** (0.15 mmol) and the corresponding nitrile NCR (0.16 mmol) in toluene (20 mL) was stirred for several days until total disappearance of the starting dihydride compound. After filtration of the solution through Cellite to eliminate solid decomposition products, the solvent was evaporated to dryness. Although the complexes containing bridging dppm (except **4b**) were easily crystallized from toluene/petroleum ether at −20 °C, it was not possible to obtain crystals for the complexes having a tedip bridge (except in the case of **3d**) because of their high solubility in organic solvents. Anal. Calc for $C_{34}H_{27}NO_6P_2Mn_2$ (**3b**, red-orange crystals, 63%): C, 56.93; H, 3.79; N, 1.95. Found: C, 57.12; H, 3.78; N, 1.93. Calc for $C_{16}H_{23}NO_{11}P_2Mn_2$ (**3d**, red-orange powder, 68%): C, 33.29; H, 4.01; N, 2.43. Found: C, 33.41; H, 3.99; N, 2.40. Calc for $C_{19}H_{29}NO_{11}P_2Mn_2$ (**3e**, red-orange powder, 69%): C, 36.85; H, 4.72; N, 2.26. Found: C, 36.69; H, 4.67; N, 2.24. Calc for $C_{38}H_{29}NO_6P_2Mn_2$ (**4a**, yellow crystals, 70%): C, 59.47; H, 3.81; N, 1.82. Found: C, 59.71; H, 3.83; N, 1.79. Calc for $C_{39}H_{31}NO_6P_2Mn_2$ (**4b**, yellow powder, 53%): C, 59.94; H, 4.00; N, 1.79. Found: C, 60.11; H, 4.02; N, 1.73. Calc for $C_{41}H_{35}NO_6P_2Mn_2$. (**4c**·toluene, orange crystals, 76%): C, 60.83; H, 4.35; N, 1.73. Found: C, 61.10; H, 4.45; N, 1.69. The toluene proportion in the crystals was determined from the ^{1}H NMR spectrum. Anal. Calc for $C_{34}H_{26}N_2O_6P_2Mn_2$ (**4d**, orange crystals, 77%): C, 55.91; H, 3.59; N, 3.83. Found: C, 56.11; H, 3.62; N, 4.00. Calc for $C_{21}H_{27}NO_{11}P_2Mn_2$ (**4e**, yellow powder, 78%): C, 39.34; H, 4.24; N, 2.18. Found: C, 39.51; H, 4.27; N, 2.12. Calc for $C_{17}H_{25}NO_{11}P_2Mn_2$ (**4f**, yellow powder, 77%): C, 34.54; H, 4.26; N, 2.37. Found: C, 34.37; H, 4.30; N, 2.31.

Preparation of Complexes 5a,b and 6. The procedure followed in the preparation of these complexes is quite similar to that described for the synthesis of complexes **3b,d,e** and **4a–f**, and therefore, it is not further explained. The complex **5a** was recrystallized from toluene/petroleum ether at −20 °C, and **6**, from diethyl ether/hexane at −20 °C. Anal. Calc for $C_{36}H_{31}NO_6P_2Mn_2$ (**5a**, yellow crystals, 83%): C, 58.00; H, 4.19; N, 1.88. Found: C, 58.25; H, 4.27; N, 1.90. Calc for $C_{19}H_{29}NO_{11}P_2Mn_2$ (**5b**, yellow powder, 66%): C, 36.86; H, 4.72; N, 2.26. Found: C, 36.71; H, 4.66; N, 2.12. Calc for $C_{39}H_{31}NO_6P_2Mn_2$ (**6**, yellow crystals, 67%): C, 59.94; H, 4.00; N, 1.79. Found: C, 60.15; H, 4.06; N, 1.71.

Preparation of [$Mn_2(\mu,\eta^1,\eta^2$-CN-4-$CH_3C_6H_4)(CO)_6(\mu$-tedip)] (5c). After the addition of 0.022 g (0.188 mmol) of CN-4-$CH_3C_6H_4$ to a red violet solution of **2** (0.1 g, 0.186 mmol) in toluene (20 mL) the mixture turned yellow instantaneously. Solvents were then removed, and the residue was chromatographied at −30 °C through an alumina column (activity IV, 8 × 2.5cm). Elution with petroleum ether gave a yellow band, which yielded, after removal of the solvent in vacuum, compound **5c** (44%). Elution with petroleum ether/toluene (10/1) gave a mixture of products which could neither be further separated nor be identified. Analytical pure samples of the complex **5c** could not be obtained.

X-ray Data Collection, Structure Determination, and Refinement for Compounds 3a and 4a. Crystals of both compounds were of small size and of very poor quality. The crystals selected for the X-ray analyses diffracted weakly, especially that of **3a**, so that very accurate structure determinations were prevented. The crystallographic data are summarized in Table III. Unit cell parameters were determined from the θ values of 30 (**3a**) and 28 (**4a**) carefully centered reflections, having $9.0 < \theta < 14.9°$ (**3a**) and $10.5 < \theta < 14.6°$ (**4a**). Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the niobium-filtered Mo Kα radiation and the $\theta/2\theta$ scan type. The reflections for both **3a** and **4a** were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.60)°$ to $(\theta + 0.60 + 0.346 \tan \theta)°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.[17] Intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied. Only the observed reflections were used in the structure solutions and refinements.

Table III. Experimental Data for the X-ray Diffraction Studies

	3a	4a
mol formula	$C_{33}H_{25}Mn_2NO_6P_2$	$C_{38}H_{29}Mn_2NO_6P_2$
mol wt	703.39	767.47
cryst system	orthorhombic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$
radiatn (λ, Å)	Nb-filtered Mo Kα (0.71073)	
a, Å	14.444 (5)	14.285 (6)
b, Å	19.965 (7)	12.028 (6)
c, Å	11.207 (5)	10.902 (6)
α, deg	90	86.74 (3)
β, deg	90	105.32 (2)
γ, deg	90	97.59 (2)
V, Å^3	3232 (2)	1790 (2)
Z	4	2
D_{calcd}, g cm^{-3}	1.446	1.424
$F(000)$	1432	784
cryst dimens, mm	0.13 × 0.18 × 0.24	0.20 × 0.23 × 0.28
μ(Mo Kα), cm^{-1}	8.90	8.10
2θ range, deg	6–48	6–48
reflecns measd	h,k,l	$\pm h,\pm k,l$
no. of unique tot. data	2881	5900
no. of unique obsd data	1179 [$I > 2\sigma(I)$]	2118 [$I > 2\sigma(I)$]
R	0.0537	0.0626
R_w	0.0693	0.0738

Table IV. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 3a

atom	x/a	y/b	z/c
Mn(1)	9244 (2)	4895 (1)	1651 (3)
Mn(2)	7914 (2)	4061 (2)	473 (3)
P(1)	10324 (3)	4036 (3)	1766 (5)
P(2)	8883 (4)	3126 (3)	524 (5)
O(1)	10291 (12)	5480 (8)	−344 (15)
O(2)	10173 (10)	5608 (7)	3637 (13)
O(3)	8019 (11)	6100 (8)	1525 (15)
O(4)	6549 (13)	5135 (10)	318 (18)
O(5)	6500 (10)	3228 (8)	−647 (16)
O(6)	8789 (13)	4585 (8)	−1747 (15)
N	8327 (11)	4307 (7)	2220 (12)
C(1)	9917 (15)	5235 (11)	450 (21)
C(2)	9840 (15)	5331 (10)	2832 (20)
C(3)	8421 (14)	5612 (11)	1591 (21)
C(4)	7126 (16)	4753 (11)	428 (20)
C(5)	7090 (17)	3548 (12)	−208 (19)
C(6)	8454 (16)	4371 (12)	−850 (24)
C(7)	7626 (14)	3943 (10)	2293 (18)
C(8)	7023 (16)	3674 (11)	3252 (21)
C(9)	10120 (12)	3345 (9)	687 (16)
C(10)	10474 (12)	3633 (9)	3255 (17)
C(11)	11201 (13)	3160 (10)	3401 (19)
C(12)	11250 (17)	2813 (11)	4497 (24)
C(13)	10567 (15)	2994 (11)	5420 (22)
C(14)	9950 (15)	3463 (11)	5258 (18)
C(15)	9871 (13)	3785 (9)	4146 (16)
C(16)	11540 (13)	4309 (10)	1427 (19)
C(17)	12014 (16)	4617 (11)	2369 (20)
C(18)	12930 (16)	4875 (12)	2070 (21)
C(19)	13233 (16)	4784 (12)	971 (22)
C(20)	12831 (17)	4431 (12)	74 (20)
C(21)	11940 (16)	4187 (12)	272 (20)
C(22)	8976 (13)	2602 (9)	−804 (18)
C(23)	9487 (14)	1987 (11)	−744 (20)
C(24)	9577 (15)	1585 (11)	−1805 (22)
C(25)	9151 (17)	1796 (13)	−2831 (22)
C(26)	8596 (15)	2380 (12)	−2906 (21)
C(27)	8539 (14)	2781 (11)	−1873 (21)
C(28)	8637 (15)	2485 (11)	1677 (22)
C(29)	9296 (15)	2276 (11)	2533 (20)
C(30)	8984 (17)	1823 (13)	3423 (24)
C(31)	8010 (18)	1568 (11)	3328 (23)
C(32)	7417 (17)	1747 (14)	2516 (24)
C(33)	7702 (14)	2223 (11)	1655 (22)

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[17] Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A.* 1974, *30*, 580.

Table V. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 4a

atom	x/a	y/b	z/c
Mn(1)	1640 (2)	3795 (2)	991 (2)
Mn(2)	3586 (2)	3776 (2)	877 (2)
P(1)	1854 (3)	2684 (4)	2866 (4)
P(2)	3914 (3)	2579 (3)	2666 (4)
O(1)	1209 (8)	5646 (11)	2346 (11)
O(2)	−400 (9)	2713 (11)	228 (13)
O(3)	1171 (10)	5298 (11)	−1281 (13)
O(4)	5130 (8)	2868 (10)	66 (11)
O(5)	3320 (9)	5292 (11)	−1401 (13)
O(6)	4972 (9)	5559 (11)	2403 (11)
N	2309 (8)	2893 (9)	56 (11)
C(1)	1380 (11)	4903 (12)	1826 (14)
C(2)	390 (12)	3145 (13)	532 (15)
C(3)	1381 (12)	4668 (14)	−420 (17)
C(4)	4499 (12)	3210 (15)	380 (15)
C(5)	3393 (11)	4695 (15)	−520 (17)
C(6)	4443 (14)	4848 (15)	1812 (17)
C(7)	1918 (14)	2159 (16)	−789 (17)
C(8)	2361 (12)	1597 (14)	−1603 (16)
C(9)	1966 (20)	502 (18)	−1907 (20)
C(10)	2408 (20)	−207 (21)	−2592 (22)
C(11)	3219 (18)	332 (19)	−2966 (20)
C(12)	3559 (17)	1394 (19)	−2754 (15)
C(13)	3166 (12)	2084 (20)	−2056 (15)
C(14)	1283 (12)	3129 (14)	4034 (15)
C(15)	1785 (12)	3537 (13)	5204 (16)
C(16)	1303 (15)	3867 (15)	6034 (19)
C(17)	304 (15)	3757 (13)	5748 (21)
C(18)	−204 (15)	3357 (16)	4573 (19)
C(19)	255 (12)	3024 (14)	3713 (19)
C(20)	1437 (12)	1200 (15)	2821 (18)
C(21)	1292 (12)	597 (14)	1758 (19)
C(22)	1039 (13)	−577 (15)	1709 (22)
C(23)	884 (15)	−1156 (21)	2742 (22)
C(24)	1027 (17)	−572 (19)	3850 (28)
C(25)	1277 (14)	590 (16)	3872 (20)
C(26)	3146 (9)	2740 (14)	3729 (15)
C(27)	5148 (10)	2881 (12)	3702 (15)
C(28)	5911 (11)	2546 (14)	3286 (16)
C(29)	6846 (14)	2835 (16)	3940 (19)
C(30)	7078 (13)	3437 (16)	5037 (19)
C(31)	6357 (11)	3770 (16)	5466 (18)
C(32)	5413 (12)	3515 (13)	4801 (15)
C(33)	3837 (8)	1093 (10)	2491 (12)
C(34)	3914 (9)	358 (12)	3547 (14)
C(35)	3859 (9)	−776 (13)	3421 (15)
C(36)	3777 (11)	−1266 (15)	2217 (17)
C(37)	3674 (11)	−577 (11)	1193 (16)
C(38)	3738 (8)	616 (10)	1339 (13)

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms for **4a** and excepting the carbon atoms for **3a**. The very similar values of the thermal parameters for the N and C(7) atoms (U = 0.046 and 0.044 Å^2) at the end of the isotropic refinement confirm the correct assignment of these atoms, even if the presence of the nitrile ligand is evidenced especially by the spectroscopic data (Table I). Since the space group $P2_12_12_1$ leads to a chiral configuration in the structure, an independent final cycle of refinement for **3a** was carried out using the coordinates $-x$, $-y$, $-z$ for the non-hydrogen atoms. No improvement in the R value was obtained [$R(x, y, z) = 0.0564$; $R(-x, -y, -z) = 0.0581$]. The former model was selected, and the reported data refer to this model. All hydrogen atoms [excepting for H(1) and H(7) of **4a**, clearly localized from a ΔF map and refined isotropically] were placed at their geometrically calculated positions (C–H = 1.00 Å) and introduced in the final structure factors calculation with fixed isotropic thermal parameters (**3a**) or refined "riding" the corresponding carbon atoms (**4a**). The final cycles of refinement were carried out on the basis of 232 (**3a**) and 477 (**4a**) variables; after the last cycles, no parameters shifted by more than 0.45 (**3a**) and 0.28 (**4a**) esd. The highest remaining peak in the final difference map was equivalent to about 0.42 (**3a**) and 0.78 (**4a**) e/Å^3. In the final cycles of refinement a weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.665 and 0.0109 (**3a**) and 0.734 and 0.0019 (**4a**), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 18. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna, Italy) and on the Gould Powernode 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR (Parma, Italy) using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[19] The final atomic coordinates for the non-hydrogen atoms are given in Table IV (**3a**) and Table V (**4a**). The atomic coordinates of the hydrogen atoms are given in Tables SI (**3a**) and SII (**4a**) of the supplementary material, and the thermal parameters, in Tables SIII (**3a**) and SIV (**4a**) of the supplementary material.

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Registry No. 1, 116405-31-3; **2**, 101461-94-3; **3a**, 116374-37-9; **3b**, 138208-35-2; **3c**, 138208-36-3; **3d**, 138233-97-3; **3e**, 138233-98-4; **4a**, 138208-37-4; **4b**, 138208-38-5; **4c**, 138208-39-6; **4d**, 138208-40-9; **4e**, 138233-99-5; **4f**, 138234-00-1; **5a**, 116405-33-5; **5b**, 138234-01-2; **5c**, 138234-02-3; **6**, 138208-41-0; *fac*-[Mn(H)(CO)$_3$(dppm)], 36344-24-8.

Supplementary Material Available: Tables of hydrogen atom coordinates (Tables SI and SII), thermal parameters for the non-hydrogen atoms (Tables SIII and SIV), and complete bond distances and angles (Table SV and SVI) (10 pages); listings of observed and calculated structure factors (Tables SVII and SVIII) (20 pages). Ordering information is given on any current masthead page.

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(18) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(19) Sheldrick, G. M. SHELX-76 Program for crystal structure determination. University of Cambridge, England, 1976. Sheldrick, G. M. SHELXS-86 Program for the solution of crystal structures. University of Göttingen, 1986.