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ISOCYANIDE ADDITION TO $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$ AND THE FORMATION OF A FOUR-ELECTRON DOUBLY-BRIDGING ISOCYANIDE

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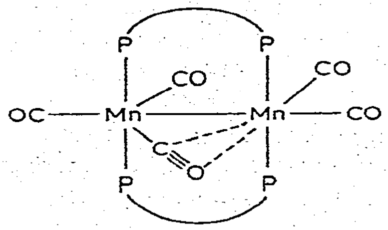
Summary

Addition of RNC (R = p-$CH_3C_6H_4$, $C_6H_5CH_2$, or CH_3) to $Mn_2(CO)_5(dpm)_2$ (dpm = $Ph_2PCH_2PPh_2$) produces $Mn_2(CO)_5(CNR)(dpm)_2$ with a terminal isocyanide. Heating of this complex produces $Mn_2(CO)_5(dpm)_2$ (R = CH_3 or $C_6H_5CH_2$) or $Mn_2(CO)_4(CNR)(dpm)_2$ (R = p-$CH_3C_6H_4$). The latter probably contains a four-electron doubly-bridging isocyanide ligand.

Introduction

In recent years the bonding modes of carbon monoxide ligands have proven to be extremely versatile. In addition to the well-established terminal, doubly-bridging, and triply-bridging modes, new bonding modes involving CO as a doubly-bridging four-electron donor [1,2] and as a semi-bridging ligand [3] have been characterized. Other isoelectronic ligands, particularily isocyanides, may be expected to participate in similar modes of coordination. Added impetus for study of such novel forms of ligand—metal coordination comes from the suggestion that (1) multiple metal bonding of carbon monoxide or dinitrogen may weaken the triple bond and render this bond more susceptible to facile catalytic hydrogenation [4] and that (2) bridging ligands may play a role in ligand substitutions of polynuclear organometallics [5].

Here are described the results of a study of isocyanide addition to $Mn_2(CO)_5(dpm)_2$ (I) (dpm = $Ph_2PCH_2PPh_2$). Complex I possesses a carbon monoxide ligand which serves as a conventional two electron σ donor toward one manganese atom and as a two electron π donor toward the second manganese atom [1].



(I)

Experimental

Commercial samples of $Mn_2(CO)_{10}$ (Strem) and benzyl isocyanide (Aldrich) were used as received. Methyl isocyanide [6] and *p*-tolyl isocyanide [7] were prepared by standard methods. $Mn_2(CO)_5(dpm)_2$ was prepared as described in the literature [1]. All preparations were performed in degassed solvents under an atmosphere of purified nitrogen.

Infrared spectra were recorded on a Beckman IR-12 spectrometer. Proton magnetic resonance spectra were recorded on a JEOL JNM-MH-100 spectrometer. Melting points were taken in capillaries sealed under nitrogen.

$Mn_2(CO)_5(dpm)_2(p\text{-}CH_3C_6H_4NC)$. *p*-Tolyl isocyanide was added to a stirred suspension of 0.41 g (0.40 mmol) of $Mn_2(CO)_5(dpm)_2$ in 20 ml of dichloromethane until dissolution was complete. The solution was concentrated under vacuum and the product was precipitated by addition of hexane. Recrystallization from dichloromethane/hexane, followed by vacuum drying at 78°C, resulted in pure yellow-orange crystalline product (yield 0.40 g, 83%). M.p. 184—187°C. (Found: C, 66.10; H, 4.48; N, 1.61. $Mn_2C_{63}H_{51}N_1O_5P_4$ calcd.: C, 66.61; H, 4.53; N, 1.23%.)

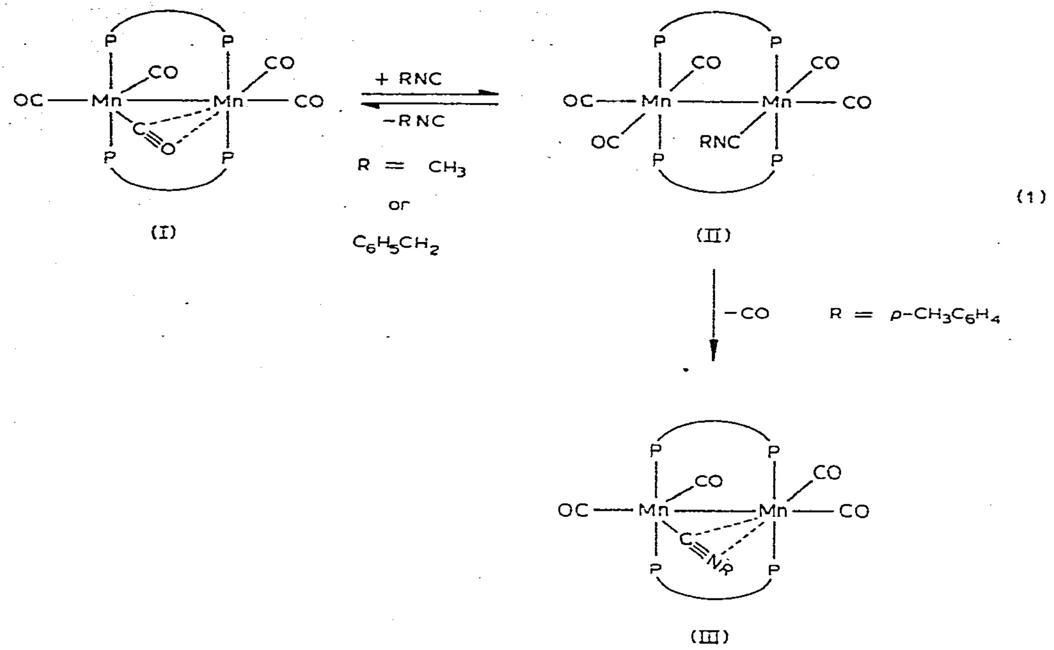
$Mn_2(CO)_5(dpm)_2(C_6H_5CH_2NC)$. Using benzyl isocyanide in place of *p*-tolyl isocyanide, the yellow product was synthesized, recrystallized, and dried as described above to give product in 77% yield. The PMR spectrum indicates that dichloromethane and hexane remain occluded in the complex even after several days of vacuum drying at 78°C. This fractional amount of solvent results in a higher carbon and hydrogen content than the following calculated values indicate. M.p. 179—182°C. (Found: C, 67.39; H, 4.72; N, 1.25. $Mn_2C_{63}H_{51}N_1O_5P_4$ calcd.: C, 66.61; H, 4.53; N, 1.23%).

$Mn_2(CO)_5(dpm)_2(CH_3NC)$. As described above, the product was synthesized using methyl isocyanide and purified to give yellow crystals in 52% yield. M.p. 178—181°C. (Found: C, 64.74; H, 4.72; N, 1.25. $Mn_2C_{57}H_{47}N_1O_5P_4$ calcd.: C, 64.60; H, 4.47; N, 1.32%.)

$Mn_2(CO)(dpm)_2(p\text{-}CH_3C_6H_4NC)$. A *p*-xylene solution of $Mn_2(CO)_5(dpm)_2$-(p-$CH_3C_6H_4NC$) (0.20 g) was refluxed for 3 hours, concentrated under vacuum and refrigerated. The resulting precipitate was filtered and washed with several portions of hexane. Pure yellow-orange crystals were obtained by recrystallization from dichloromethane/hexane followed by vacuum drying at 78°C (yield 0.15 g, 77%.) M.p. >250°C. (Found: C, 67.60; H, 5.04; N, 1.35; P, 11.49. $Mn_2C_{62}H_{51}N_1O_4P_4$ calcd.: C, 67.21; H, 4.64; N, 1.26; P, 11.18%.)

Results and discussion

Our results may be readily summarized by eq 1. Isocyanide addition to I is particularily facile. When an isocyanide (methyl, benzyl or *p*-tolyl) is added dropwise to a slurry of I in dichloromethane at 23°C, the complex dissolves over a 30 minute period. Concentration of the solution under vacuum followed by addition of hexane yields yellow-orange products, II. Spectroscopic data pertinent to the characterization of II are presented in Table 1. In particular, the incorporation of a terminal isocyanide ligand is indicated by the observation of a terminal infrared ν(CN) band at ca. 2070—2140 cm^{-1} and by observation of resonances of the isocyanide ligand in the proton magnetic resonance spectrum.



(1)

Heating II, when the isocyanide ligand bears a methyl or benzyl substituent, in *p*-xylene solution for three hours results in the reformation of I in 50—70% yield. The spectroscopic data clearly identify I as the product and verify the absence of any isocyanide ligand in it. In contrast, under similar conditions II (R = *p*-$CH_3C_6H_4$) loses carbon monoxide to form III. Spectroscopic data for III are shown in Table 1. The proton magnetic resonance spectrum clearly indicates that a *p*-tolyl group is present in the product. The PMR spectra of II and III with

TABLE 1

SPECTROSCOPIC DATA

Complex	Infrared data (cm^{-1}) [a]		Proton magnetic resonance data [b]	
	ν(CO)	ν(CN)	CH_2(dpm)	Isocyanide ligand
$Mn_2(CO)_6(dpm)_2$ [c]	1987vw, 1923(sh), 1912s, 1866m	—	3.70	
$Mn_2(CO)_5(dpm)_2$	1940m, 1902s, 1862, 1832m, 1648m	—	3.51	
$Mn_2(CO)_5(dpm)_2(p\text{-}CH_3C_6H_4NC)$	1946s, 1901s, 1872m, 1847s	2071m	3.71	2.29(CH_3); 6.89, 6.42 (J(HH), 0.8 Hz) C_6H_4 AB quartet
$Mn_2(CO)_5(dpm)_2(C_6H_5CH_2CN)$	1947m, 1900s, 1869m, 1846m	2123m	3.72	3.56(CH_2)
$Mn_2(CO)_5(dpm)_2(CH_3NC)$	1943m, 1898s 1867s, 1838m	2138m	3.72	2.17(CH_3)
$Mn_2(CO)_4(dpm)_2(p\text{-}CH_3C_6H_4NC)$	1936m, 1892s, 1857s, 1825m	1661m	3.24	2.20(CH_3); 6.90, 6.70 (J(HH), 0.8 Hz) C_6H_4 AB quartet

[a] Dichloromethane solution. [b] Chloroform-*d* solution (ppm downfield from TMS). [c] Ref. 1.

p-tolyl isocyanide are shown in Fig. 1. No CN stretching frequency characteristic of a terminal CN unit is observed in the infrared spectrum. Rather, III shows a strong band at 1661 cm^{-1} which is assigned to a bridging isocyanide ligand. This ν(CN) occurs at lower energies than found for well-characterized doubly-bridging, two-electron-donating isocyanide ligands [8]. By analogy with I, III is formulated as containing a four-electron doubly-bridging ligand.

Complex III is unreactive toward further addition reactions. It does not react with p-tolyl or methyl isocyanide, either at 23°C after 7 days, or at elevated temperatures. Complex III may gain some stability from favorable overlap of the phenyl rings of the isocyanide and phosphine ligands. The PMR spectrum of III in Fig. 1 contains evidence of some close phenyl—phenyl contacts. The PMR spectrum of II shows a pattern of two broad aromatic resonances at 7.5 and 7.2 ppm. This is the pattern we have observed for a large number of metal—dpm complexes in chloroform. However, in III the aromatic resonances are much more widely spaced with additional features occurring at 6.4 and 8 ppm. We suggest that the shifts of these aromatic resonances are caused by ring current effects resulting from the close face to face association of the phenyl groups of the isocyanide and dpm ligands.

Our results indicate that a single isomer of II has been obtained. From both the transformations of II into I or III and the knowledge that CO scrambling between manganese atoms in I is not particularly facile [8], we conclude that II is formed as the equatorial isomer. If an axial isocyanide ligand were present in II, one would expect that terminal isocyanides would be found in products resulting from thermolysis of II. Consequently, in the present case the formation of a four-electron doubly-bridging carbon monoxide ligand in I does facili-

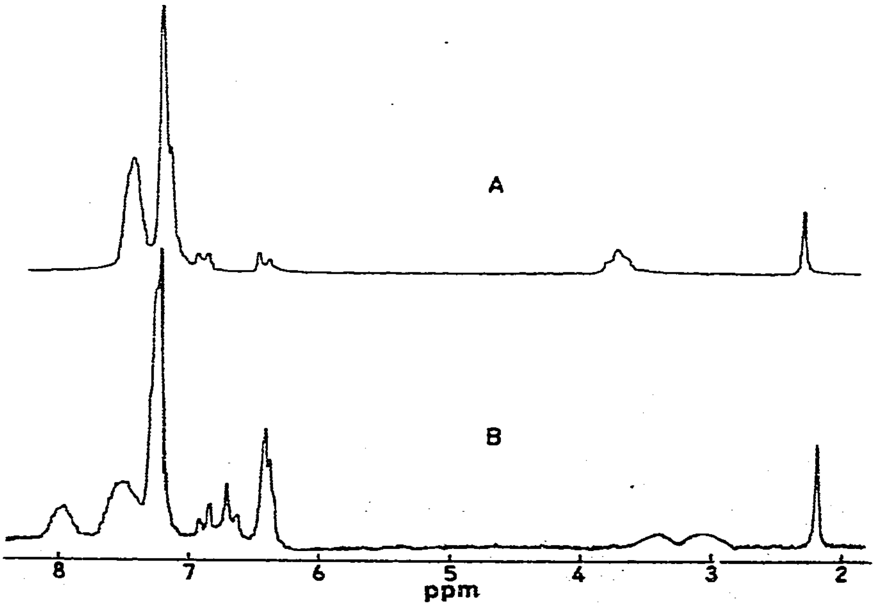
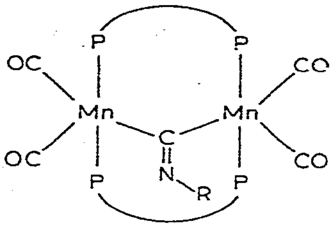


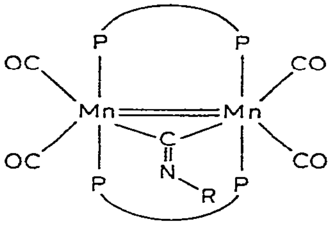
Fig. 1. PMR spectra of the p-tolyl isocyanide complexes in chloroform-d solution: (A) $Mn_2(CO)_5(dpm)_2$-(p-$CH_3C_6H_4NC$), (B) $Mn_2(CO)_4(dpm)_2$(p-$CH_3C_6H_4NC$).

tate substitution into a dimanganese carbonyl complex but, contrary to the suggested scheme of Atwood and Brown [5], it does not lead to axial substitution.

By analogy with I, and the observation of an unusually low value of ν(CN) for a bridging isocyanide, structure III is certainly the most likely structure for $Mn_2(dpm)_2(CO)_4(p\text{-}CH_3C_6H_4NC)$. However, two other structures, IV and V, are not wholly inconsistent with the data available for this material.



(IV)



(V)

Structure IV would lack a Mn—Mn bond and would be analogous to the structure which we have recently determined for $Pd_2(dpm)_2(CNCH_3)_3^{2+}$ [10]. Such structures produce a 16 electron count at each metal, a situation which is clearly more common for four-coordinate palladium than for manganese. Structure V would involve the formation of a Mn—Mn double bond. No precedent has been set for the formation of such a species although it, as well as structure III, produces an electron-precise species. Consequently a crystallographic determination of the structure of $Mn_2(dpm)_2(CO)_4(p\text{-}CH_3C_6H_4NC)$ is in progress.

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