A Structural and Kinetic Investigation of the Isomers of $M_2(CO)_8(CNBu^t)_2$ (M = Mn, Re)

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The kinetic product of the catalysed reaction between $Mn_2(CO)_{10}$ and Bu^tNC, 1,2-$Mn_2(CO)_8(CNBu^t)_2$, isomerizes on heating to the 1,1 isomer which has been characterized by *X*-ray crystallography.

The mechanism of the reaction of $M_2(CO)_{10}$ (M = Mn, Re) with donor ligands L (*e.g.* L = phosphine) to give $M_2(CO)_{10-x}L_x$ (x = 1, 2) has been a topic of much controversy,[1—3] only recently resolved by isotopic labelling studies.[4,5] However, questions relating to the geometries of the kinetic and thermodynamic products have still to be resolved[3] and herein we report our results on the reaction of $M_2(CO)_{10}$ (M = Mn, Re) with Bu^tNC which provides information on this problem.

The reaction of $Mn_2(CO)_{10}$ (1 mmol) with Bu^tNC (2 equiv.) in benzene (10 ml) in the presence of PdO (10 mg) as catalyst at 50 °C results in a rapid reaction to yield crude $Mn_2(CO)_8(CNBu^t)_2$.[6] The crude complex was purified by column chromatography (silica gel, eluant hexane) and recrystallisation from hexane (−5 °C) yielded a first crop of material (isomer A, Figure 1) characterized by elemental analyses, mass spectrometry [M^+ 500 and fragments at m/z 305(100%) and 221(96) corresponding to $Mn(CO)_3(CNBu^t)_2^+$ and $Mn(CNBu^t)_2^+$, respectively], and finally *X*-ray crystallography.† An ORTEP diagram of the molecule is shown in Figure 2. Important points relating to this structure are as follows. (i) The structure reveals an unusual *cis* arrangement of Bu^tNC ligands on the *same* metal.[7] (ii) The two halves of the molecule are staggered with respect to each other and *both* the CO and Bu^tNC ligands bend in towards the

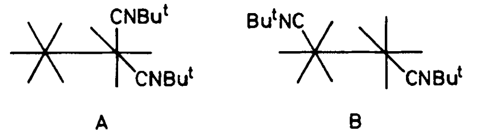

Figure 1. Two isomers of $M_2(CO)_8(CNBu^t)_2$ (M = Mn, Re).

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† *Crystal data* for $Mn_2(CO)_8(CNBu^t)_2$ isomer A: $Mn_2C_{18}H_{18}N_2O_8$, M_r = 500.21, yellow rectangular crystals obtained from pentane (−5 °C), a = 20.535(8), b = 12.291(5), c = 9.289(4) Å, β = 90.38(3)°, U = 2344 Å^3, Z = 4, D_c = 1.42 g cm^{-3}, μ = 10.71 cm^{-1}, space group $P2_1/n$, Mo-K_α radiation, R = R_w = 0.0563, $F(000)$ = 1519.94, scan mode ω–2θ, $3 \leq \theta \leq 26$, 4178 measured intensities, 3798 unique reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. I.r. spectroscopic data for the dimer complexes.[a]

		νNC/cm^{-1}	νCO/cm^{-1}
$Mn_2(CO)_8(CNBu^t)_2$	(A)	2165(w), 2136(w)	2055(m), 1999(vs), 1977(s), 1964(w), 1952(m), 1934(m)
$Mn_2(CO)_8(CNBu^t)_2$	(B)	2144(w)	2049(w), 2006(s), 1977(vs), 1943(sh), 1939(m)
$Re_2(CO)_8(CNC_6H_3Me_2$-2,6$)_2$		2166(m), 2124(m)	2053(m), 2028(s), 1985(vs), 1943(w), 1938(s)
$Re_2(CO)_8(CNBu^t)_2$[b]		2155(m)	2059(w), 2024(m), 1979(vs) — 1934(m)

[a] Recorded in hexane; m = medium, s = strong, w = weak, vs = very strong, sh = shoulder. [b] ^{1}H N.m.r. (benzene): single resonance at δ 0.87.

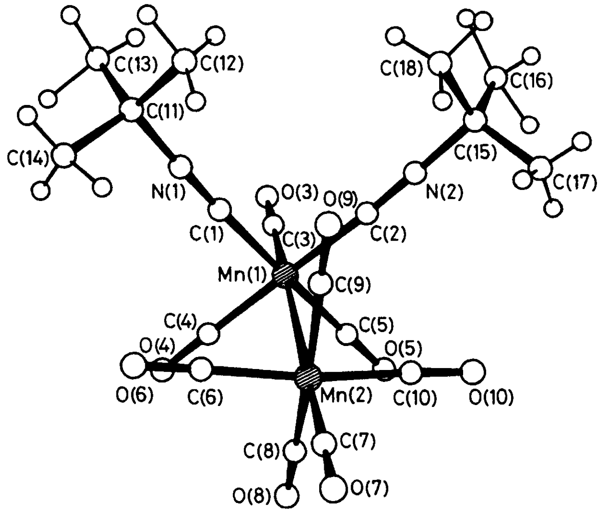

Figure 2. The molecular structure of 1,1-$Mn_2(CO)_8(CNBu^t)_2$ (isomer A). Selected average bond lengths (Å), Mn–CO$_{ax}$ 1.748(5), Mn–CO$_{eq}$ (*trans* to CO) 1.841(5), Mn–CO$_{eq}$ (*trans* to CNBu^t) 1.824(5), Mn–CN 1.944(4). Selected average bond angles (°), C$_{ax}$–Mn–C$_{eq}$ 94.2(2), C$_{eq}$–Mn–C$_{eq}$ 89.6(2), Mn–Mn–C$_{eq}$ 85.9(2), Mn–C–O 177.9(4), Mn–C–N 177.6(4), C–N–C 176.7(4).

centre of the molecule.[8] (iii) The Mn–Mn bond length [2.924(1) Å] is longer than that observed for $Mn_2(CO)_{10}$ [2.904(1) Å][9] and suggests that the changed σ/π bonding capacity of the Bu^{t}NC ligand (relative to CO) or steric factors perturb the Mn–Mn distance.

Repeated recrystallisation (−5 °C, hexane) of the purified $Mn_2(CO)_8(CNBu^t)_2$ yielded a second disubstituted complex (5th crop) with an i.r. spectrum quite different from that of isomer A (Table 1).[6] The i.r. spectrum is, however, very similar to that of $Re_2(CO)_8(CNC_6H_3Me_2$-2,6$)_2$ for which preliminary *X*-ray crystallographic data[10] indicate a structure corresponding to isomer B (Figure 1).

An i.r. kinetic investigation in hexane of the synthesis and interconversion of the isomers of $Mn_2(CO)_8(CNBu^t)_2$ has revealed the following. (i) The PdO catalysed synthesis of $Mn_2(CO)_8(CNBu^t)_2$ from $Mn_2(CO)_9(CNBu^t)$ and excess of Bu^{t}NC at 25 °C yields *only* isomer B. (ii) For both the catalysed and uncatalysed reaction of $Mn_2(CO)_{10}$ with Bu^{t}NC, the monosubstituted product is formed more rapidly than the disubstituted product (*e.g.* catalysed reaction $k_{mono} = 1.3 \times 10^{-2}\,s^{-1}$, $k_{di} = 6.3 \times 10^{-4}\,s^{-1}$). (iii) The isomerization reaction A → B was found to be unimolecular (independent of reactant concentration; Table 2) and non-dissociative (independent of added Bu^{t}NC). (iv) The isomerisation reaction occurs at a measurable rate when $T > 50\,°C$ ($t_{\frac{1}{2}}$ at 53 °C *ca.* 130 min) with $\Delta H^\circ = -7.44\,kJ\,mol^{-1}$ and $\Delta S^\circ = -20\,J\,mol^{-1}\,K^{-1}$ (Table 2).

The data for $Mn_2(CO)_8(CNBu^t)_2$ suggest that isomer B is the kinetic product of the reaction and that isomer A is only slowly formed subsequently in an isomerisation reaction.

Table 2. Kinetic data for the isomerization A ⇌ B.[a]

T/°C	k_f/s^{-1}	k_r/s^{-1}	*K*
53	8.8×10^{-5}	5.9×10^{-5}	1.5
72[b]	4.5×10^{-4}	3.5×10^{-4}	1.3
72[c]	4.8×10^{-4}	3.9×10^{-4}	1.3
84	1.2×10^{-3}	9.9×10^{-4}	1.2

[a] Reaction monitored by i.r. spectroscopy using absorptions at 2006 and 1999 cm^{-1}. [b] $Mn_2(CO)_8(CNBu^t)_2 = 2.96 \times 10^{-3}\,mol\,l^{-1}$. [c] $Mn_2(CO)_8(CNBu^t)_2 = 4.95 \times 10^{-3}\,mol\,l^{-1}$.

Further, the above results suggest that the reaction $Mn_2(CO)_9(CNBu^t) + Bu^tNC \rightarrow Mn_2(CO)_8(CNBu^t)_2$ proceeds with displacement of a CO from the unsubstituted metal, and not *via cis*-labilization of a CO on the same metal[11] followed by transfer of the unsaturation to the second metal.[3] This is further substantiated by kinetic data for the reaction $Mn_2(CO)_8(CNBu^t)_2 + Bu^tNC \rightarrow Mn_2(CO)_7(CNBu^t)_3$. The reaction proceeds more *slowly* than for the catalysed synthesis of $Mn_2(CO)_8(CNBu^t)_2$ from $Mn_2(CO)_9(CNBu^t)$, *and* isomer A reacts more rapidly than isomer B (isomer A, $k = 3.6 \times 10^{-3}\,s^{-1}$, isomer B, $k = 1.4 \times 10^{-3}\,s^{-1}$) to form the trisubstituted product.

Preliminary data on the PdO catalysed reaction of $Re_2(CO)_{10}$ with Bu^{t}NC (25 °C, benzene) to yield $Re_2(CO)_8(CNBu^t)_2$ have revealed the presence of only isomer B by i.r. and n.m.r. spectroscopy (Table 1). Attempts to obtain isomer A by thermal interconversion (125 °C, octane, 8 h) have been unsuccessful and this suggests that isomer B (the kinetic product of the reaction) is separated by a high energy barrier from isomer A.

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