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# MIXED METAL DIMERS

## I. THE REACTION OF $[MnRe(CO)_{10}]$ WITH ISOCYANIDES

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## Summary

The PdO catalysed reaction between $[MnRe(CO)_{10}]$ and RNC (R = ${}^iPr$, ${}^tBu$, 2,6-$Me_2C_6H_3$, $C_6H_{11}$) readily gave the Re monosubstituted derivatives $[MnRe(CO)_9(CNR)]$ in high yield. The Mn substituted derivative $[Mn(CO)_4(CN{}^tBu)Re(CO)_5]$ was synthesized by an indirect route. No thermal interconversion between the two isomers was observed.

## Introduction

The thermal reaction between $[M_2(CO)_{10}]$ (M = Mn, Re) and L (L = isocyanide, phosphines, phosphites) to give $[M_2(CO)_{10-x}L_x]$ ($x$ = 1,2) has been shown to occur via a dissociative process which does not involve metal–metal bond cleavage [1–5]. Similar observations have been reported for the reaction between $[MnRe(CO)_{10}]$ and $PPh_3$, $P(OPh)_3$ and $PBu_3$ [3]. A consideration of the kinetic data for the reaction of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ with L [1,6] suggests that substitution of CO by L on $[MnRe(CO)_{10}]$ should occur on the Mn atom in the mixed dimer. However, the Re substituted product is obtained as the major product in the reaction [3,7]. This result has been rationalized by Sonnenberger and Atwood [3] and involves transfer of unsaturation between metal centres as indicated in Fig. 1.

Herein we report on the reaction of $[MnRe(CO)_{10}]$ with isocyanides which we anticipated would provide further information on the site preference of the substitution process. Isocyanides were chosen as they have a small cone angle [8] and their ability to bridge metal centres should provide further information on the transfer of unsaturation between metal centres. To date the chemical reactivity of $[MnRe(CO)_{10}]$ has been little studied and only a limited number of substituted derivatives of the

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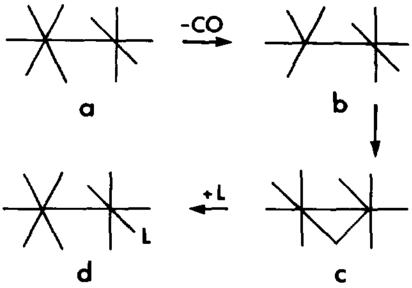

Fig. 1. Sonnenberger–Atwood mechanism for ligand substitution on [MnRe(CO)$_{10}$].

dimer are known [9]. This study represents a continuation of our own interest in the site specific ligand substitutions of metal dimers [10] and linear (acylic) clusters [11].

## Experimental

[MnRe(CO)$_{10}$] was synthesized by the literature procedure [12]. All the isocyanides and the PdO catalyst were used as purchased and all solvents were dried and degassed before use. Reactions were routinely performed under nitrogen.

IR spectra were recorded on a Jasco IRA 1, or a Perkin–Elmer 580B spectrophotometer, mass spectra on a Varian Mat CH7 spectrometer (operating at 70 eV), and NMR spectra on a Bruker WP80 spectrometer.

Kinetic reactions, monitored by IR spectroscopy, were carried out in the dark under an inert atmosphere in n-hexane or i-octane. Stirring rate was constant throughout the reactions studied and temperature stability was ±1°C.

### *Synthesis of [MnRe(CO)$_9$(CNR)] (R = $^i$Pr, $^t$Bu, 2,6-Me$_2$C$_6$H$_3$, C$_6$H$_{11}$)*

To a stirred solution of [MnRe(CO)$_{10}$] (1 mmol) and PdO as catalyst (10 mg) in hexane (50 ml) was added RNC (1.1 mmol). The solution was stirred under nitrogen and the reaction monitored by IR spectroscopy or thin layer chromatography (silica; hexane/benzene mixtures). The reactions were complete within 4 h as judged by IR spectroscopy. The required yellow complexes were purified by recrystallisation from a hexane solution at −5°C. IR and NMR spectral data for the new complexes are given in Table 1 *.

### *Synthesis of [Mn(CO)$_4$(CN$^t$Bu)Re(CO)$_5$]*

[Mn(CO)$_4$(CN$^t$Bu)Mn(CO)$_4$(CN$^t$Bu)] (1 mmol), synthesized from Mn$_2$(CO)$_{10}$ and $^t$BuNC in the presence of PdO as catalyst [13,14], was added dropwise in tetrahydrofuran (30 ml) to a sodium amalgam (Na, 4 mmol; Hg, 5 ml) under nitrogen. [Re(CO)$_5$Br] (1.1 mmol) in tetrahydrofuran (30 ml) was added to the filtered solution of Na[Mn(CO)$_4$(CN$^t$Bu)] and the mixture stirred overnight at room temperature. Solvent removal followed by ether extraction of the crude product yielded the required dimer which was recrystallised from hexane at −5°C. IR and NMR spectral data are recorded in Table 1 *.

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* Satisfactory elemental analyses have been obtained for all compounds.

*Isomerisation studies on [MnRe(CO)$_9$(CN$^t$Bu)]*

Isomerisation studies were performed in i-octane solutions under an inert atmosphere at a known constant stirring rate. No isomerisation was observed after 8 h for the reactions carried out at $\leq 95$°C in the dark.

## Results and discussion

[MnRe(CO)$_{10}$] was synthesized by the literature procedure [12] in yields approaching 70%. Traces of [Mn(CO)$_{10}$] were generally found as an impurity in the final reaction product but no attempt was made to separate this impurity from [MnRe(CO)$_{10}$] in the synthetic reactions. This impurity together with [MnRe(CO)$_{10}$] reacted rapidly with RNC in the presence of catalyst (PdO) [10]. The substituted products [MnRe(CO)$_9$(CNR)] and [Mn$_2$(CO)$_{10-x}$(CNR)$_x$] ($x = 1, 2$) formed in the reactions could readily be separated by chromatography (silica) or fractional crystallisation.

In the absence of catalyst no reaction was observed between [MnRe(CO)$_{10}$] and RNC (25°C, 6 h). The effect of the catalyst is thus to reduce the activation energy barrier for the reaction and enable the reaction to proceed under very mild conditions. The reaction in the presence of catalyst was allowed to proceed until all the starting material had been consumed. At this stage little if any disubstituted product had been formed. The synthesis of the disubstituted product [MnRe(CO)$_8$(CNR)$_2$] requires more forcing conditions [15].

The products [MnRe(CO)$_9$(CNR)] were characterized by IR and $^1$H NMR spectroscopy (Table 1) and elemental analyses. All data are consistent with the formation of a monosubstituted derivative of [MnRe(CO)$_{10}$]. However, the data did not differentiate between the numerous possible isomers that could have formed nor whether an isomeric mixture was obtained from the synthesis. From a knowledge of the bonding properties of the RNC ligand [10] equatorial substitution was expected. Two isomers are thus possible (see Fig. 2).

An X-ray crystal structure determination was thus performed on the [MnRe(CO)$_9$(CN$^t$Bu)] derivative to determine the site of coordination of $^t$BuNC and this indicated that isomer **A** had been synthesized [15] (see below). The synthesis of the alternative isomer, isomer **B**, was thus undertaken to ascertain whether physical and spectroscopic properties could be used to differentiate between **A** and **B**. As indicated in Table 1, the NMR data are not helpful but the IR spectra allow the two complexes to be differentiated e.g. $\nu$(CO) at 2041 (isomer **B**) and 2055 (isomer **A**). A knowledge of the IR spectra of the two isomers **A** and **B** thus indicates that the exclusive isomer formed in the catalysed reaction (monitored by IR spectroscopy) is isomer **B**.

Attempts to interconvert the isomers thermally were unsuccessful (i-octane, 95°C, 8 h). This implies that isomer **B** is formed directly in the substitution reaction and not by formation of **A** and rapid rearrangement to isomer **B**. Isomer interconversion has been previously observed for [Mn$_2$(CO)$_8$(CN$^t$Bu)$_2$] but not [Re$_2$(CO)$_8$(CN$^t$Bu)$_2$] [14]. Metal–metal bond cleavage followed by dimer reformation [16] is also ruled out by the lack of any homonuclear substituted and unsubstituted dimers that would be expected from such a radical mechanism.

Kinetic data for the reaction of [M$_2$(CO)$_{10}$] (M$_2$ = Mn$_2$, Re$_2$, MnRe) with $^t$BuNC in the presence of PdO as catalyst were obtained. Reactions were carried out

TABLE 1

PHYSICAL AND SPECTRAL DATA FOR THE MONOSUBSTITUTED METAL DIMERS [MM′(CO)$_9$(CNR)] (M, M′ = Mn, Re)

| Complex | M.p. (°C) [a] | IR (cm$^{-1}$) [b] | | NMR [c] (δ,ppm) |
|---|---|---|---|---|
| | | ν(NC) | ν(CO) | |
| [Mn$_2$(CO)$_9$(CN$^t$Bu)] [d] | 91– 92 | 2170m | 2092m, 2032s, 1996vs, 1968m, 1958s | 0.77 |
| [Re$_2$(CO)$_9$(CN$^t$Bu)] [e] | 104–106 | 2173m | 2101m, 2050s, 2018sh, 1996vs, 1979w, 1970m, 1952s | 0.75 |
| [Mn(CO)$_5$Re(CO)$_4$(CN$^t$Bu)] | 101–102 | 2182w | 2090m, 2041s, 2024w, 2002vs, 1977m, 1963s, 1957s | 0.75 |
| [Mn(CO)$_4$(CN$^t$Bu)Re(CO)$_5$] | 92– 93 | 2180w | 2099m, 2055s, 2018w, 2000vs, 1979m, 1971s, 1954s | 0.76 |
| [MnRe(CO)$_9$(CN$^i$Pr)] | 71– 72 | 2187w | 2089m, 2040s, 2030w, 2005vs, 1978m, 1963s, 1957s | 0.54(d), 2.99(m) [f] |
| [MnRe(CO)$_9$(CNC$_6$H$_3$Me$_2$-2,6)] | 109–110 | 2154w | 2083m, 2042s, 2026w, 2004vs, 1988w, 1966s, 1960s | 1.96(s), 6.54(m) [g] |
| [MnRe(CO)$_9$(CNC$_6$H$_{11}$)] [h] | – | 2189w | 2093m, 2047s, 2032w, 2002vs, 1980m, 1964s, 1957s | 0.75–1.35 [i] |

[a] Uncorrected. [b] Recorded in hexane. [c] Recorded in C$_6$D$_6$ relative to TMS. [d] Ref. 12. [e] Ref. 8. [f] Signal ratio 6/1. [g] Signal ratio 2/1. [h] Oily solid. [i] Complex multiplet.

(A) (B)

Fig. 2. Isomers of [MnRe(CO)$_9$(CN$^t$Bu)].

under pseudo-first order conditions (20-fold excess of $^t$BuNC) and the values for the rate constant obtained at 25°C are given in Table 2. It is apparent from this data that the catalysed reaction of [Mn$_2$(CO)$_{10}$] and [Re$_2$(CO)$_{10}$] with $^t$BuNC occur at comparable rates but that the reaction with [MnRe(CO)$_{10}$] is anomalous. Indeed, when the rate constant is assessed on the basis of the number of equatorial CO groups on the type of substituted metal atom ($k'$, Table 2) then the reaction of the mixed dimer is more rapid than with the homonuclear dimers. However, a significant feature is that under our catalysed reaction conditions the rate of reaction of $^t$BuNC with [Mn$_2$(CO)$_{10}$] and [Re$_2$(CO)$_{10}$] are very similar. The substitution of CO on [MnRe(CO)$_{10}$] by isocyanides could occur at either the Re or Mn atom (according to the rate data) on the homonuclear dimers but the product obtained is exclusively the Re substituted derivative. Two explanations could be suggested to account for the preferential substitution of Re in the product.

Firstly, loss of CO could occur from the Mn atom. This could be followed by the formation of a CO bridged intermediate (symmetrical or unsymmetrical) in which the bridging CO is supplied by the Re atom. Attack of the dimer by the incoming ligand now occurs preferentially at the Re atom (Fig. 1) [3]. Steric factors have been suggested to rationalize this type of site selectivity in other dimers and clusters [17] but this argument seems unlikely for the sterically undemanding RNC ligands.

An alternative explanation involving loss of CO from the Re atom is also possible. This could be rationalized in terms of *cis*-labilization arguments [18] and would suggest that Mn(CO)$_5$ is a better *cis*-labilizing group than Re(CO)$_5$. This proposal would imply that the RNC ligand attaches itself to the same metal (Re) which loses the CO ligand. Studies to differentiate between the above two mechanisms are presently underway.

Finally, it should be mentioned that a number of other derivatives of [MnRe(CO)$_{10}$] have been synthesized. Direct and indirect syntheses of formyl and

TABLE 2

KINETIC DATA FOR THE REACTION OF [MM′(CO)$_{10}$] (M, M′ = Mn, Re) WITH Bu$^t$NC USING PdO CATALYST

| Complex | $k$ [a] | $t_{1/2}$ [b] | $k'$ [a,c] |
|---|---|---|---|
| [Mn$_2$(CO)$_{10}$] | 20.89 | 6.2 (4.8) | 2.61 |
| [Re$_2$(CO)$_{10}$] | 21.99 | 3.8 (4.5) | 2.75 |
| [MnRe(CO)$_{10}$] | 16.01 | 11.7 (3.6) | 4.00 |

[a] Pseudo-first-order rate constant in s$^{-1}$ (×10$^3$). [b] Half-life for reaction (min). The figures in parentheses indicate the number of half-lives during which the reaction was monitored. [c] Rate constant per equatorial carbonyl.

carbene complexes of the type [$MnRe(CO)_9L$] (L = C(OME)Me, C(OME)$C_6H_5$ [19,20], CHO [21]) have indicated the usual equatorially substituted derivatives and in most instances it has been proposed that L resides on the Re atom.

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## References

1 H. Wawersik and F. Basolo, Inorg. Chim. Acta, 3 (1969) 113.
2 S. Schmidt, W.C. Trogler and F. Basolo, Inorg. Chem., 21 (1982) 1698.
3 D.C. Sonnenberger and J.D. Atwood, J. Am. Chem. Soc., 102 (1980) 3484.
4 A.M. Stolzenberg and E.L. Muetterties, J. Am. Chem. Soc., 105 (1983) 822.
5 N.J. Coville, A.M. Stolzenberg and E.L. Muetterties, J. Am. Chem. Soc., 105 (1983) 2499.
6 L.I.B. Haines, D. Hopgood and A.J. Poë, J. Chem. Soc. A, (1968) 421; L.I.B. Haines and A.J. Poë, J. Chem. Soc. A, (1969) 2826.
7 J.P. Fawcett and A. Poë, J. Chem. Soc., Dalton Trans., (1976) 2039; J.P. Fawcett, A. Poë and M.V. Twigg, J. Organomet. Chem., 61 (1973) 315.
8 Y. Yamamoto, K. Aoki and H. Yamazaki, Inorg. Chem., 18 (1979) 1681.
9 G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford 1982, Vol. IV.
10 See for example: G.W. Harris and N.J. Coville, Organometallics, 4 (1985) 908.
11 For a recent review of linear (acyclic) clusters see M.O. Albers, D.J. Robinson and N.J. Coville, Coord. Chem. Rev., 69 (1986) 127.
12 N. Flitcroft, D.K. Huggins and H.D. Kaesz, Inorg. Chem., 3 (1964) 1123.
13 M.O. Albers and N.J. Coville, S. Afr. J. Chem., 35 (1982) 139.
14 D.J. Robinson, G.W. Harris, J.C.A. Boeyens and N.J. Coville, J. Chem. Soc., Chem. Commun., (1984) 1307.
15 N.J. Coville and D.J. Robinson, unpublished results.
16 A.J. Poë, Trans. Met. Chem., 7 (1982) 65
17 J.D. Atwood, M.J. Wovkulich and D.C. Sonnenberger, Acc. Chem. Res., 16 (1983) 350.
18 J.D. Atwood and T.L. Brown, J. Am. Chem. Soc., 98 (1976) 3160.
19 C.P. Casey and C.R. Cyr, J. Organomet. Chem., 57 (1973) C69; C.P. Casey, C.R. Cyr, R.L. Anderson and D.F. Marten, J. Am. Chem. Soc., 97 (1975) 3053.
20 E.O. Fischer, E. Offhaus, J. Muller and D. Nöthe, Chem. Ber., 105 (1972) 3027.
21 J.A. Gladysz and W. Tam, J. Am. Chem. Soc., 100 (1978) 2545; W. Tam, M. Marsi and J.A. Gladysz, Inorg. Chem., 22 (1983) 1413.