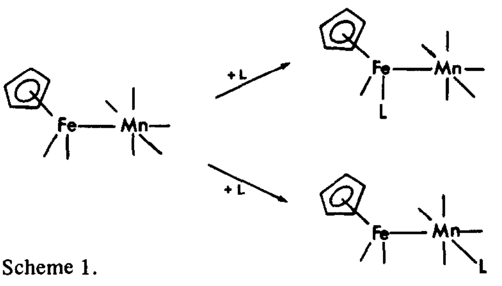
Site Selectivity Studies on Metal Dimer Complexes: The Substitution Reactions of [(η^5-C_5H_5)Fe(CO_2)-Mn(CO)$_5$]

PETER JOHNSTON, GRAHAM J. HUTCHINGS and NEIL J. COVILLE*

Chemistry Department, University of the Witwatersrand, Johannesburg, South Africa

(Received January 17, 1986)

Transition metal dimer complexes allow for a systematic study of the relative reactivities of the complex at the two metal sites. In principle it should be possible to vary the reaction conditions to achieve reactivity at either of the two metal atoms (e.g. substitution, oxidative-addition, insertion etc.) but to date no systematic studies have been reported in the literature which have explored this expectation. Indeed there are few reports on the factors which lead to reactivity at one metal rather than the other metal [1–3]. Herein we report the first of our studies in this area; the investigation of the ligand substitution reaction of mixed metal carbonyl dimers, in particular the reaction of [(η^5-C_5H_5)Fe(CO)$_2$-Mn(CO)$_5$], **A**, with isocyanides (RNC) to give the monosubstituted derivatives (Scheme 1) which indicate that these reactivity differences can be achieved.



Scheme 1.

A, synthesized by literature procedures [4], was reacted with RNC (R = ^tBu, 2,6-$Me_2C_6H_3$) in benzene at room temperature in the dark. The complexes [(η^5-C_5H_5)Fe(CO)($CNBu^t$)$_2$] [Mn(CO)$_5$] and [(η^5-C_5H_5)Fe($CNC_6H_3Me_2$-2,6)$_3$] [Mn(CO)$_5$] were rapidly formed and were isolated (70–90% yield) and characterized as their PF_6^- salts (elemental analyses; IR and NMR spectroscopy, see Table I). All attempts to increase the yields of the minor components (presumed to be monosubstituted salts and substituted dimer products; total yield

TABLE I. IR and NMR Spectroscopic Data for the New Isonitrile Complexes

	IR (cm^{-1})^a		NMR (δ, ppm)^{b,c}		
	ν(NC)	ν(CO)	C_5H_5	Me	Other
[(η^5-C_5H_5)Fe(CO)$_2$Mn(CO)$_4$($CNBu^t$)]	2153(m)	2034(m), 1971(vs), 1955(sh), 1945(s), 1920(w)	4.28	0.86	
[(η^5-C_5H_5)Fe(CO)$_2$Mn(CO)$_4$($CNC_6H_3Me_2$-2,6)]	2128(m)	2031(m), 1976(vs), 1959(sh), 1950(s), 1925(w)	4.25	2.12	6 6
[(η^5-C_5H_5)Fe(CO)($CNBu^t$)$_2$] [PF_6]	2187(s), 2166(s)	2021(s)	5 09	1.52	
[(η^5-C_5H_5)Fe($CNC_6H_3Me_2$-2,6)$_3$] [PF_6]^d	2160(m), 2115(s)		5.22	2.41	7.1
[(η^5-C_5H_5)Fe(CO)$_2$($CNBu^t$)] [BF_4]	2196(m)	2070(s), 2032(s)	5.55	1 58	
[(η^5-C_5H_5)Fe(CO)$_2$($CNC_6H_3Me_2$-2,6)] [BF_4]	2178(m)	2077(s), 2041(s)	5.68	2 45	7.2

[a] IR data recorded in hexane or CH_2Cl_2 (salts). [b] NMR data recorded in C_6D_6 or $CDCl_3$ (salts). [c] Relative to TMS. [d] This complex has been isolated previously as the I^- salt (ref. 8).

---

*Author to whom correspondence should be addressed.

approximately 5%) by varying reactant ratios, method of reagent addition, temperature etc., failed. Independently it was also shown that the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CNR)]^+$ (prepared from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, RNC and $AgBF_4$ [5]) and RNC did not occur at room temperature. Thus, substitution of CO on **A** by RNC occurs prior to $[Mn(CO)_5]^-$ displacement and hence direct reaction of RNC with **A** leads to substitution at the Fe atom of the dimer.

Reaction of **A** with NMe_3O [6] in CH_3CN rapidly resulted in the formation of an acetonitrile complex [IR (CH_3CN); 2034(m) 1958(vs) 1918(s) cm^{-1}] and addition of RNC to this complex at room temperature gave $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_4(CNR)]$ ($R = {}^tBu$, $2,6\text{-}Me_2C_6H_3$) in approximately 40% isolated yield. The new complexes were completely characterized by elemental analyses, IR and NMR spectroscopy (Table I) and mass spectrometry (parent ion and fragmentation scheme). The above data did not however establish unequivocally the site of ligand substitution. This was established by thermal (60–80 °C) and photochemical (Hanovia 100 W lamp, room temperature) decomposition of the substituted dimers in benzene which was monitored by NMR and IR spectroscopy and cleanly yielded only $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[Mn_2(CO)_8(CNBu^t)_2]$ [7]. The NMe_3O route thus yields the Mn substituted derivative. This was further confirmed by the attempted synthesis of the substituted dimers via metathetical reactions of appropriate monometallic complexes. Thus (a) reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNBu^t)I]$ [8] and $Na[Mn(CO)_5]$ did not give the required product but instead a range of (identified) complexes which included $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[Mn_2(CO)_8(CNBu^t)_2]$; (b) reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and $Mn(CO)_4(CNBu^t)]Na$ gave only $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[Mn_2(CO)_8(CNBu^t)_2]$; and (c) reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]Na$ and $[Mn(CO)_4(CNBu^t)Br]$ gave a moderate (30%) yield of $[(\eta^5\text{-}C_5H_5)FeMn(CO)_4(CNBu^t)]$. This complex had IR and NMR data identical to that of the complex obtained from the NMe_3O route and further, photolytic decomposition yielded only the expected $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[Mn_2(CO)_8(CNBu^t)_2]$ products.

All the above data are consistent with the following rationalisation. Reaction of RNC with **A** yields a complex proposed from the reactivity studies to be $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)Mn(CO)_5]$. In the presence of RNC this dimer rapidly reacts at Fe to ultimately yield salt products. Alternatively in the absence of other ligands (e.g. RNC) the complex cleaves to form radicals which recombine to form the homonuclear dimers (the thermodynamically favoured products [9]) either prior to or after the RNC migrates from Fe to Mn (see (a) above). By contrast the NMe_3O route yields a Mn substituted product in which a more stable metal RNC bond is formed and in this dimer metal–metal bond cleavage occurs in preference to RNC transfer to Fe.

Reaction of **A** with $P(OMe)_3$ and $PMePh_2$ either directly or in the presence of NMe_3O gave results entirely consistent with the above reaction scheme. However, in this instance the NMe_3O reaction e.g. with $PMePh_2$ does not yield $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_4(PMePh_2P)]$ but rather $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and diax-$[Mn_2(CO)_8(PMePh_2)]$ [10].

We have also extended our studies to the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ [11] and isocyanides. The PdO catalysed reaction [12] between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Re(CO)_5]$ and ${}^tBuNC$ (THF, 25 °C) readily yields a monosubstituted derivative in high yield. This complex, characterized by elemental analysis and spectroscopic techniques has an IR spectrum identical to that of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mn(CO)_4(CNR)]$ suggesting that substitution has taken place at the Re atom. Further studies on the investigation of the reactivity pattern of the Fe–Re dimer are in progress.

Acknowledgements

We thank the C.S.I.R. and the University for financial support.

References

1 D. Sonnenberger and J. D. Atwood, *J. Am. Chem. Soc., 102,* 3484 (1980).

2 D. J. Robinson, E. A. Darling and N. J. Coville, *J. Organomet. Chem.*, submitted for publication.

3 E. Sappa, A. Tiripicchio and P. Braunstein, *Coord. Chem. Rev., 65,* 219 (1985).

4 R. B. King, P. M. Treichel and F. G. A. Stone, *Chem. Ind.*, 747 (1961).

5 D. L. Reger and C. Collman, *J. Organomet. Chem., 131,* 153 (1977).

6 T-Y. Luh, *Coord. Chem. Rev., 60,* 255 (1984).

7 M. O. Albers and N. J. Coville, *S. Afr. J. Chem., 35,* 139 (1982).

8 M. O. Albers, E. Singleton and N. J. Coville, *J. Chem. Soc., Dalton Trans.*, 947 (1983).

9 T. Madach and H. Vahrenkamp, *Chem. Ber., 113,* 2675 (1980).

10 M. Laing, T. Ashworth and P. Sommerville, *J. Chem. Soc., Chem. Commun.*, 1251 (1972).

11 T. Blackmore, J. D. Cotton, M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A,* 2931 (1968); A. N. Nesmeyanov, G. G. Dvoryantseva, Y. N. Sheinker, N. E. Kolobova and K. N. Anisimov, *Dokl. Akad. Nauk SSSR, 169,* 843 (1966).

12 M. O. Albers and N. J. Coville, *Coord. Chem. Rev., 53,* 227 (1984).