Zwitterionic Adducts from Trialkylphosphine and (η-Allyl)dicarbonylnitrosyliron Complexes: Structure and Reactivity

Giuseppe Cardaci
Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

The reaction between [Fe(η-C_3H_5)(CO)$_2$(NO)] and strong basic phosphine ligands L [PMe_3, PEt_3, $PBu^n{}_3$, or P(C_6H_{11})$_3$] in organic solvents (benzene or diethyl ether) gives the zwitterionic adducts [Fe(η^2-CH_2=$CHCH_2PR_3$)(CO)$_2$(NO)]. The structure has been assigned on the basis of i.r. and n.m.r. spectra and conductivity measurements. The reactivity and the decomposition mechanism are discussed.

The reaction of nucleophiles with organic molecules co-ordinated to metals is extensively used in organometallic chemistry [1] as a way of synthesizing organic compounds. Recently Trost *et al.*[2] have developed a catalytic process with Pd compounds which activates the allylic carbon and allows the formation of a carbon–carbon bond in the reaction with carbanions. Extensive studies on the mechanism of this reaction have ascertained that the catalytic reaction is due to an allylic complex of Pd^{II} and that the nucleophile attack is localized on the allylic group; up to date, however, no intermediate improving this type of attack has been observed.

Other allylic complexes with various metals can be proposed as possible catalysts in the reaction of nucleophiles with the organic moiety; these have been discussed recently.[3] The allylic complex [Fe(η-C_3H_4X)(CO)$_2$(NO)] (X = H or halogen) is a good candidate for this reaction because of the strong electron-withdrawing effect of the nitrosyl ligand which makes the allyl group a powerful electrophile.[4] The electrophilicity of the allyl group in this complex is further supported by the electrochemical reduction, which is localized on the allylic ligand.[5]

In order to isolate the intermediates of the nucleophilic attack on the allylic ligand, in this work we have studied the reaction of [Fe(η-C_3H_4X)(CO)$_2$(NO)] and trialkylphosphines which act as good nucleophiles in reactions with co-ordinated organic moieties.[6]

Some results relative to this reaction have been presented in a preliminary communication.[7]

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer; ^1H n.m.r. spectra were recorded on a JEOL-CHL-60 spectrometer using $SiMe_4$ as reference. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. The analysis of iron was performed using a standard u.v. spectrophotometric method; complexes were decomposed with HCl, reduced with hydrazine, and reacted with 1,10-phenanthroline. The u.v. measurements were carried out with a Beckman DU-2 spectrophotometer.

All the complexes described in this work react quickly with oxygen either in the solid state or in solution; therefore all the operations were carried out in solvent carefully deaerated with nitrogen and the solids were stored at −25 °C. The solvents were purified following standard methods. The complexes [Fe(η-C_3H_4X)(CO)$_2$(NO)] (X = H, 1-Cl, 2-Cl, or 2-Br) were prepared following the literature methods.[8] Trimethylphosphine was prepared following the method of Wolfsberger and Schmidbaur [9] and tricyclohexylphosphine following that of Issleib and Brack.[10] All the other phosphine ligands were obtained from Fluka.

[Fe(η^2-CH_2=$CHCH_2PMe_3$)(CO)$_2$(NO)] (1).—A solution of PMe_3 (1 mol dm^{-3}, 20 cm^3) in diethyl ether was added at room temperature to a solution of [Fe(η-C_3H_5)(CO)$_2$(NO)] (0.7 g) in diethyl ether (10 cm^3). A dusty and spongy red-orange precipitate was immediately obtained. The solid was filtered off, washed repeatedly with diethyl ether until the solvent was colourless, and then dried with nitrogen; yield 0.430 g, 30% (Found: C, 37.55; H, 5.7; Fe, 21.8; N, 5.2. Calc. for $C_8H_{14}FeNO_3P$: C, 37.1; H, 5.45; Fe, 21.6; N, 5.4%).

[Fe(η-C_3H_5)(CO)(NO)(PMe_3)] (1a).—The liquor obtained after the separation of (1) was evaporated and a dark red liquid obtained. The liquid was purified by chromatography on Al_2O_3, using n-hexane–dichloromethane (80 : 20 v/v) as eluant (Found: C, 42.5; H, 5.7; N, 5.5. Calc. for $C_7H_{14}FeNO_2P$: C, 42.4; H, 5.55; N, 5.5%).

[Fe(η^2-CH_2=$CHCH_2PEt_3$)(CO)$_2$(NO)] (2).—A solution of [Fe(η-C_3H_5)(CO)$_2$(NO)] (1.0 g) in diethyl ether reacted instantaneously with PEt_3 (1 g) and a red solid was obtained (0.95 g). The solid was dried with a stream of nitrogen; yield 70% (Found: C, 44.2; H, 7.05; Fe, 18.5; N, 4.3. Calc. for $C_{11}H_{20}FeNO_3P$: C, 43.85; H, 6.7; Fe, 18.55; N, 4.65%). This reaction can be carried out in benzene also.

[Fe(η^2-CH_2=$CHCH_2PBu^n{}_3$)(CO)$_2$(NO)] (3).—A solution of [Fe(η-C_3H_5)(CO)$_2$(NO)] (1.0 g) in diethyl ether was reacted with $PBu^n{}_3$ (2 g) at room temperature. After a short induction period (2 min) the formation of a red solid was observed. It was filtered off, washed with diethyl ether, and dried with nitrogen (yield 60%). The dry solid is pyrophoric (Found: C, 52.45; H, 8.45; Fe, 14.6; N, 3.50. Calc. for $C_{17}H_{32}FeNO_3P$: C, 53.0; H, 8.35; Fe, 14.5; N, 3.65%). The solution obtained after the separation of (3) showed similar CO stretching frequencies in the i.r. spectrum to the complex [Fe(η-C_3H_5)(CO)(NO)($PBu^n{}_3$)], previously described.[8c]

[Fe{η^2-CH_2=$CHCH_2P(C_6H_{11})_3$}(CO)$_2$(NO)] (4).—[Fe(η-C_3H_5)(CO)$_2$(NO)] (1 g) was added to a solution of P(C_6H_{11})$_3$ (2.5 g) in diethyl ether (ligand : complex molar ratio = 1.5 : 1). Immediately the formation of a red spongy solid was observed. The solid was filtered off and washed with diethyl ether; yield 1.2 g, 50% (Found: C, 60.5; H, 8.55; Fe, 11.8; N, 2.95. Calc. for $C_{23}H_{38}FeNO_3P$: C, 59.6; H, 8.25; Fe, 12.0; N, 3.0%).

[Fe{η^2-CHCl=$CHCH_2P(C_6H_{11})_3$}(CO)$_2$(NO)] (5).—[Fe(η-1-ClC_3H_4)(CO)$_2$(NO)] (0.5 g) was added to a solution of P(C_6H_{11})$_3$ (5 g) in toluene at 0 °C (molar ratio 10 : 1); immediately a red solid was obtained. It was washed with toluene, then diethyl ether, and dried with nitrogen; yield 0.4 g, 30% (Found: C, 55.8; H, 7.3; Fe, 11.3; N, 3.0. Calc. for $C_{23}H_{27}ClFeNO_3P$: C, 55.5; H, 7.5; Fe, 11.2; N, 2.8%).

With a ligand : complex ratio of <8 : 1 the separation of a red oil, showing the CO stretching frequencies of the anion

$[Fe(CO)_3(NO)]^-$, was observed. Formation of the red oil was also observed when the reaction was carried in diethyl ether, however high the ligand : complex ratio.

Reaction between $[Fe(\eta\text{-}C_3H_4X)(CO)_2(NO)]$ (X = 2-Cl *or* 2-Br) *and* PMe_3.—$[Fe(\eta\text{-}C_3H_4X)(CO)_2(NO)]$ (X = 2-Cl or 2-Br) (1 g) was added to 50 cm^3 of a diethyl ether solution of PMe_3 (1 mol dm^{-3}). Immediately a red-grey solid was separated, which decomposes during the filtration.

Preparation of the Allylphosphonium Salts.—The following allylphosphonium salts were prepared: $[CH_2{=}CHCH_2PMe_3]Br$ (6a), $[CH_2{=}CHCH_2PEt_3]Br$ (6b), $[CH_2{=}CHCH_2P(C_6H_{11})_3]Br$ (6c), and $[CH_2{=}CHCH_2PMe_3]Cl$ (6d). The method is similar for all the compounds. Diethyl ether solutions of PR_3 and of allyl halides C_3H_5X were mixed at room temperature. From the solution the salts precipitated as white solids. The solids were filtered off, washed with diethyl ether, and dried [Found for (6a): C, 36.4; H, 7.35. Calc. for $C_6H_{14}BrP$: C, 36.55; H, 7.15%. Found for (6b): C, 45.0; H, 8.3. Calc. for $C_9H_{20}BrP$: C, 45.2; H, 8.45%. Found for (6c): C, 63.0; H, 9.7. Calc. for $C_{21}H_{38}BrP$: C, 62.85; H, 9.55%. Found for (6d): C, 38.4; H, 7.1. Calc. for $C_6H_{13}Cl_2P$: C, 38.55; H, 7.0%].

Stability of the Complexes (1)—(5).—Complexes (1), (2), and (3) are soluble in highly polar organic solvents (acetonitrile, acetone, *etc.*). The complexes (4) and (5) are slightly soluble in the above polar solvents. The solutions of (1)—(5) in acetonitrile show slow decomposition with formation of $[Fe(CO)_3(NO)]^-$ salts and other products not characterized. If the solution is saturated with carbon monoxide the decomposition rate is increased and only the formation of $[Fe(CO)_3(NO)]^-$ salts is observed.

Conductivity Measurements.—Conductivity measurements were carried at 25 °C with an Amel conductometer, using a cell with platinized platinum electrodes and cell constant of 0.94 cm. The variation in the conductivity of a solution of (1) (9.21×10^{-4} mol dm^{-3}) in CH_3CN was measured against time. The initial conductivity was 14 μS (Λ_M = molar conductivity = 16 S cm^2 mol^{-1}). This value increased slowly up to 140 μS when the formation of the $[Fe(CO)_3(NO)]^-$ salt was complete (Λ_M = 162 S cm^2 mol^{-1}). With a stream of nitrogen the final value of conductivity was reached more quickly. This is due, perhaps, to decomposition catalyzed by the platinum electrodes. A similar trend of the conductivity measurements was observed with the complexes (2)—(4) and in various solvents (acetone, acetone–water mixtures).

Results and Discussion

The reaction of neutral phosphine nucleophiles (L) with $[Fe(\eta\text{-}C_3H_4X)(CO)_2(NO)]$ has been studied previously;[8c,11] it

Table 1. Carbonyl and NO stretching frequencies of $[Fe(\eta^2\text{-}CHX{=}CYCH_2PR_3)(CO)_2(NO)]$

Compd.	X	Y	R	Solvent	ν_{CO}/ cm^{-1}	ν_{NO}/ cm^{-1}
(1)	H	H	CH_3	Nujol	1 926, 1 834	1 586
				CH_3CN	1 933, 1 852	1 616
(2)	H	H	C_2H_5	Fluorolube	1 922, 1 821	1 572
				CH_3CN	1 935, 1 855	1 625
(3)	H	H	C_4H_9	Nujol	1 921, 1 838	1 610
(4)	H	H	C_6H_{11}	Nujol	1 927, 1 852	1 614
				Fluorolube	1 929, 1 850	1 607
				KBr	1 930, 1 845	1 610
(5)	Cl	H	C_6H_{11}	Fluorolube	1 944, 1 872	1 623
				KBr	1 946, 1 868	1 627

Table 2. Hydrogen-1 n.m.r. spectra of $[Fe(\eta^2\text{-}CH^aH^b{=}CH^cCH_2PR_3)(CO)_2(NO)]$ in CD_3CN and of $[CH^aH^b{=}CH^cCH_2PR_3]X$ in $CDCl_3$ *

Compound	X	$\delta(H^{a,b,c})$/p.p.m.	Relative intensity	$\delta(CH_2)$/p.p.m.	Relative intensity	δ(R)/p.p.m.	Relative intensity
(1)		3.29 (m), 2.55 (s), 2.54 (s)	3	2.20 (dd) $J(CH_2\text{–}P)$ = 15 $J(CH_2\text{–}H^c)$ = 5.2	2	1.87 (d) $J(CH_3\text{–}P)$ = 14.2	9
(2)		3.12 (m), 2.58 (s), 2.51 (s)	3	Obscured by R		$\delta(CH_3)$ = 1.15 (dt) $J(CH_3\text{–}P)$ = 18 $J(CH_3\text{–}CH_2)$ = 7.8 $\delta(CH_2)$ = 2.29 (dq) $J(CH_2\text{–}P)$ = 12.7	9 6 + 2
(3)		3.04 (m), 2.5 (s), 2.34 (s)	3	Obscured by R		0.84, 1.44, 2.29	27 + 2
(6a)	Br	5.8—5.3 (m)	3	3.58 (dd) $J(CH_2\text{–}P)$ = 16.5 $J(CH_2\text{–}H^c)$ = 6	2	2.21 (d) $J(CH_3\text{–}P)$ = 14.5	9
(6b)	Br	5.6—5.1 (m)	3	3.52 (dd) $J(CH_2\text{–}P)$ = 15 $J(CH_2\text{–}H^c)$ = 5.7	2	$\delta(CH_3)$ = 1.34 (dt) $J(CH_3\text{–}P)$ = 17.5 $J(CH_3\text{–}CH_2)$ = 7.5 $\delta(CH_2)$ = 2.54 (dq) $J(CH_2\text{–}P)$ = 12.7	15
(6c)	Br	5.9—5.0 (m)	3	3.76 (dd) $J(CH_2\text{–}H^c)$ = 6.8 $J(CH_2\text{–}P)$ = 16.5	2	$\delta(C_6H_{10})$ = 1.88, 1.51 δ(CH) = 4.29	30 3
(6d)	Cl	5.9—5.4 (m)	2	3.99 (d) $J(CH_2\text{–}P)$ = 16.5	2	2.08 (d) $J(CH_2\text{–}P)$ = 15	9

* *J* Values are in Hz; q = quartet. R = Me, Et, Bu^n, or C_6H_{11}.

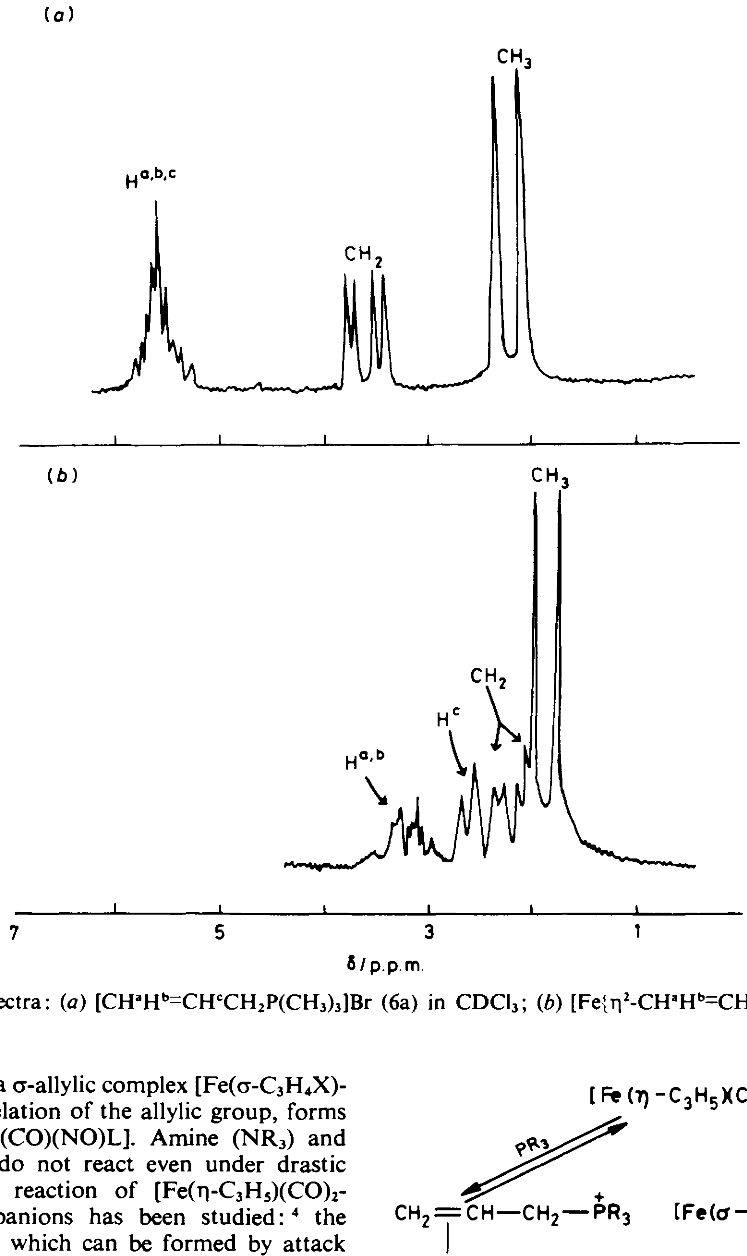
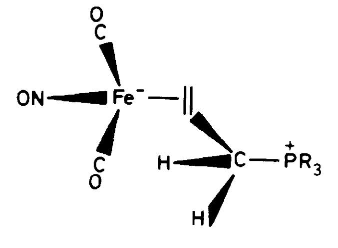
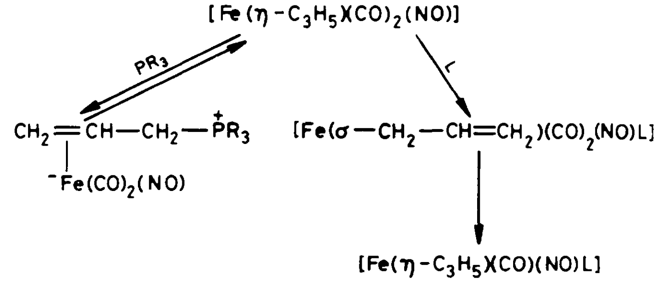


Figure. Hydrogen-1 n.m.r. spectra: (*a*) $[CH^aH^b{=}CH^cCH_2P(CH_3)_3]Br$ (6a) in $CDCl_3$; (*b*) $[Fe\{\eta^2\text{-}CH^aH^b{=}CH^cCH_2P(CH_3)_3\}(CO)_2(NO)]$ (1) in CD_3CN

proceeds with formation of a σ-allylic complex $[Fe(\sigma\text{-}C_3H_4X)(CO)_2(NO)L]$ which, by chelation of the allylic group, forms the complex $[Fe(\eta\text{-}C_3H_4X)(CO)(NO)L]$. Amine ($NR_3$) and arsine ($AsPh_3$) derivatives do not react even under drastic conditions.[12] Recently the reaction of $[Fe(\eta\text{-}C_3H_5)(CO)_2(NO)]$ with stabilized carbanions has been studied:[4] the formation of intermediates, which can be formed by attack of the nucleophile on the allyl ligand, was observed.

When L = PMe_3, PEt_3, $P(C_6H_{11})_3$, or PBu^n_3 rapid formation of red spongy solid, very sensitive to oxygen and to heat, is observed in weakly polar or non-polar solvents (diethyl ether, benzene, toluene). The dry solids are pyrophoric. Repeated attempts at crystallization, using various polar and non-polar solvent mixtures were unsuccessful. Therefore, on the basis of the spectroscopic results (i.r. and ^1H n.m.r.; Tables 1 and 2), of the conductivity measurements, and of the elemental analyses, the zwitterionic structure was assigned to complexes (1)—(5). The ^1H n.m.r. spectrum of complex (1) [Figure (*b*)] shows the presence of a phosphonium group,[13] an upfield shift[14] of *ca.* 2.5 p.p.m. for the vinyl group $CH_2{=}CH$ compared with the corresponding allylphosphonium salt [Figure (*a*)], and a double doublet for the CH_2 allylic group due to the coupling with the phosphorus and with the vinyl CH. The i.r. spectra show two CO stretching bands of equal intensity in the range 1 940—1 830 cm^{-1} and one NO stretching band in the range 1 630—1 580 cm^{-1} (Table 1). The shift of *ca.* 100 cm^{-1} in the CO and NO stretching bands compared with the σ-allylic complexes[11] suggests that the iron atom is negatively charged. On the other hand, the initial equivalent conductivity is very low in agreement with the absence of ions





Scheme. L = PR_3, $P(OR)_3$, $P(OPh)_3$, or PPh_3; R = Me, Et, Bu^n, or C_6H_{11}

and consistent with an overall neutral, charge-separated zwitterionic formulation.

Recently a few examples of zwitterionic adducts formed by direct nucleophilic attack on uncharged hydrocarbon π complexes of neutral Group 5B and 4B ligands have been described.[15,16] In these cases the charge separation is assisted by a polynuclear structure. It is not so common to find examples of mononuclear dipolar ions: the compound $PMe_3CH_2BH_3^-$ (ref. 17) and some derivatives of molybdenum and tungsten recently described [18] are examples of this structure. Zwitterionic structures due to the interaction of phosphine ligands with allylic complexes have been proposed in the literature [19] to explain reaction mechanisms. The easy formation of the complexes (1)—(5) in spite of their reactivity is due to the absence of an ionizable group and to the quick separation from the solution owing to their low solubility in non-polar solvents.

The reactivity of the $[Fe(\eta\text{-}C_3H_5X)(CO)_2(NO)]$ complexes with neutral nucleophiles can be summarised by the Scheme. When the phosphine ligands are very basic the zwitterionic adducts are formed; with phosphites $[P(OMe)_3$ or $P(OPh)_3]$ and triphenylphosphine, only the substitution reaction is observed. In some cases both reaction pathways are active ($L = PMe_3$ or PBu^n_3).

Acknowledgements

This work was supported by C.N.R. and M.P.I. grants.

References

1 P. L. Pauson, *J. Organomet. Chem.*, 1980, **200**, 207; J. Tsuji, *Acc. Chem. Res.*, 1969, **2**, 144; 1973, **6**, 8.

2 B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; B. M. Trost, L. Weber, P. E. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3416, 3426.

3 S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.

4 J. L. A. Roustan and F. Houlihan, *Can. J. Chem.*, 1979, **57**, 2790; J. L. A. Roustan, J. Y. Merour, and F. Houlihan, *Tetrahedron Lett.*, 1979, **39**, 3721.

5 G. Paliani, S. M. Murgia, and G. Cardaci, *J. Organomet. Chem.*, 1971, **30**, 221.

6 R. Salzer, *Inorg. Chim. Acta*, 1976, **17**, 221; L. A. P. Kane-Maguire and D. A. Sweigart, *Inorg. Chem.*, 1979, **18**, 700.

7 G. Cardaci, *J. Organomet. Chem.*, 1980, **202**, C81.

8 (*a*) M. D. Murdoch, *Z. Naturforsch., Teil. B*, 1965, **20**, 179; (*b*) R. Bruce, F. M. Chaudari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 1967, 2255; (*c*) G. Cardaci and A. Foffani, *J. Chem. Soc., Dalton Trans.*, 1974, 1808.

9 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal Org. Chem.*, 1974, **4**, 149.

10 K. Issleib and A. Brack, *Z. Anorg. Allg. Chem.*, 1954, **277**, 258.

11 G. Cardaci, *J. Chem. Soc., Dalton Trans.*, 1974, 2472.

12 G. Cardaci, S. M. Murgia, and A. Foffani, *J. Organomet. Chem.*, 1972, **37**, C11; G. Cardaci and S. M. Murgia, *J. Organomet. Chem.*, 1970, **25**, 483.

13 M. J. Gallacher, *Aust. J. Chem.*, 1968, **21**, 1197.

14 E. Koerner Von Gustorf, M. C. Henry, and D. J. McAdoo, *Annalen*, 1967, **190**, 707; M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organomet. Chem.*, 1966, **3**, 1.

15 Y. S. Wong, H. N. Paik, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1975, 309; A. J. Carty, G. N. Mott, N. J. Taylor, and J. E. Yule, *J. Am. Chem. Soc.*, 1978, **100**, 3051.

16 K. Henrick, M. McPartin, A. J. Deeming, S. Hasso, and P. Manning, *J. Chem. Soc., Dalton Trans.*, 1982, 899.

17 H. Schmidbaur, G. Muller, B. Milewski-Mahrla, and V. Shubert, *Chem. Ber.*, 1980, **113**, 2576.

18 J. L. Davidson, G. Vasapollo, L. Manojlovic-Muir, and K. W Muir, *J. Chem. Soc., Chem. Commun.*, 1982, 1025.

19 D. A. Clark, D. L. Jonas, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1980, 565.

Received 6*th June* 1983; *Paper* 3/931