Journal of Organometallic Chemistry, 55 (1973) C24–C26
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Cationic arenechromium-nitrosyls and -hydrides

DAVID E. BALL and NEIL G. CONNELLY*
Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

(Received May 7th, 1973)

SUMMARY

Complexes $Cr(CO)_2L(C_6Me_{6-n}H_n)$, $n = 0$–3, L = CO and PPh_3, react with $NOPF_6$ in methanol/toluene to give $[Cr(CO)L(NO)(C_6Me_{6-n}H_n)]PF_6$, $n = 0$–3, L = CO; $n = 0$, L = PPh_3, and these react with nucleophiles (X^-) to give cyclohexadienyl derivatives $Cr(CO)_2(NO)(C_6Me_{6-n}H_nX)$; the compounds $Cr(CO)_2(PhC{\equiv}CPh)(C_6Me_{6-n}H_n)$ react with $NOPF_6$ to yield $[Cr(H)(CO)_2(PhC{\equiv}CPh)(C_6Me_{6-n}H_n)]PF_6$, $n = 0$ and 1.

It is well established that the nitrosonium ion (NO^+) will displace carbon monoxide from phosphine-substituted carbonyls to afford isoelectronic monocationic nitrosyls *viz.* $[M(CO)_{x-1}P_y(NO)]^+$ [1,2]. We have now shown that this type of displacement reaction occurs with metal carbonyls containing organic ligands. Apart from a limited number of π-cyclopentadienyl species[3,4] and $[Os(CO)(PPh_3)_2(NO)X]PF_6$, X = C_2H_4 [5]; X = acetylenes[6]; the new arene species reported below are the first examples of cationic organometallic nitrosyls to be prepared.

In methanol/toluene mixtures polymethylated arenechromiumtricarbonyls, $Cr(CO)_3(C_6Me_{6-n}H_n)$, $n = 0$–3, react with $NOPF_6$ to give the air-stable, yellow salts $[Cr(CO)_2(NO)(C_6Me_{6-n}H_n)]PF_6$ (I–IV)** (Table 1). This contrasts with the reaction of $Cr(CO)_3(C_6MeH_5)$ with NO^+ in acetonitrile which leads to displacement of the arene ligand[7]. Complex (I) may also be prepared by displacement of triphenylphosphine from $Cr(CO)_2(PPh_3)(C_6Me_3H_3)$, whereas the reaction between $Cr(CO)_2(PPh_3)(C_6Me_6)$ and $NOPF_6$ yields a mixture of (IV) and $[Cr(CO)(PPh_3)(NO)(C_6Me_6)]PF_6$ (V).

Attempts to prepare cationic arenechromium acetylene nitrosyls, from $Cr(CO)_2(PhC{\equiv}CPh)(C_6Me_{6-n}H_n)$, $n = 0$ and 1, and $NOPF_6$ have afforded the new maroon hydrido complexes $[Cr(H)(CO)_2(PhC{\equiv}CPh)(C_6Me_{6-n}H_n)]PF_6$ (VI–VII). The

---

* Author to whom correspondence should be addressed.
**All new compounds have satisfactory C, H and N analyses.

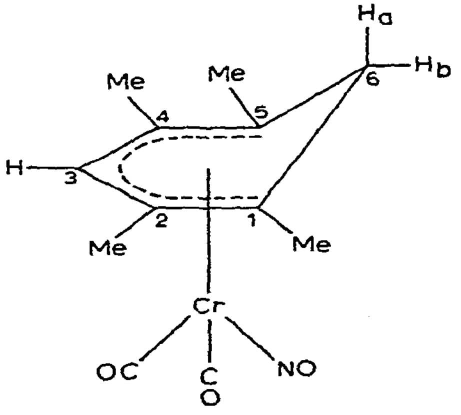
TABLE 1

	Compound[a]	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})
(I)	$[Cr(CO)_2(NO)(1,3,5\text{-}C_6Me_3H_3)]PF_6$	2073, 2027	1763
(II)	$[Cr(CO)_2(NO)(1,2,4,5\text{-}C_6Me_4H_2)]PF_6$	2072, 2026	1761
(III)	$[Cr(CO)_2(NO)(1,2,3,4,5\text{-}C_6Me_5H)]PF_6$	2066, 2019	1755
(IV)	$[Cr(CO)_2(NO)(C_6Me_6)]PF_6$	2062, 2013	1755
(V)	$[Cr(CO)(PPh_3)(NO)(C_6Me_6)]PF_6$	1980	1698
(VI)	$[Cr(H)(CO)_2(PhC{\equiv}CPh)(1,2,3,4,5\text{-}C_6Me_5H)]PF_6$	2029, 1977	
(VII)	$[Cr(H)(CO)_2(PhC{\equiv}CPh)(C_6Me_6)]PF_6$	2033, 1985	
(VIII)	$Cr(CO)_2(NO)(1,2,4,5\text{-}C_6Me_4H_3)$	2007, 1950	1687[b]
(IX)	$Cr(CO)_2(NO)(C_6Me_6H)$	2001, 1945	1683[b]
(X)	$Cr(CO)_2(NO)(1,2,4,5,6\text{-}C_6Me_5H_2)$	2005, 1947	1689[b]

[a] CH_2Cl_2 solution unless otherwise stated. [b] Hexane.

nitrosonium ion in methanol exists in equilibrium with H^+ and MeONO[8]. Presumably the increased basicity of the acetylene derivatives, over the carbonyl or phosphine analogues, causes protonation of the metal to become favoured over carbonyl displacement by NO^+. Although protonation of $Cr(CO)_2L(arene)$, L = CO and PPh_3, by CF_3CO_2H has been detected spectroscopically[9,10] the complexes reported here are the first such species to be isolated as stable crystalline solids.

The dicarbonylnitrosyl cations (I—IV) react with nucleophiles (X^-) to give neutral substituted cyclohexadienyl complexes $Cr(CO)_2(NO)(C_6Me_{6-n}H_nX)$, characterised by mass and ^1H NMR spectra and by elemental analysis. With $NaBH_4$ in tetrahydrofuran, for example, (II) affords orange $Cr(CO)_2(NO)(1,2,4,5\text{-}C_6Me_4H_3)$ (VIII) [^1H NMR: 8.72 (6) $Me_{1,5}$; 8.52 (6) $Me_{2,4}$; 7.96, 8.00 (2) $H_{a,b}$; 5.04 (1) H_3.] the mass spectrum of which shows the parent ion and sequential loss of two carbonyl and one nitrosyl ligands. The presence of ν(C—H) at 2760 cm^{-1} in the IR spectrum of (VIII) (2770 cm^{-1} in the spectrum of (IX)) suggests that *exo*-addition of H^- to the coordinated arene occurs[11,12]



(VIII)

Methyllithium reacts with the nitrosyl cations in tetrahydrofuran to afford methyl-substituted cyclohexadienyls, for example (X) from (II), although with (IV) no product could be isolated, presumably because of steric interaction between the *endo*-methyl group and the metal atom.

Although many organometallic cations are formed by proton addition to, or hydride abstraction from neutral species[13], with consequent modification of the coordinated organic ligand, generation of the nitrosyl cations by replacement of CO by NO^+ does not cause such modification. It may therefore be envisaged that nucleophilic attack on cations generated from the same neutral substrate by the two different methods will lead to products containing different coordinated organic ligands.

REFERENCES

1 B.F.G. Johnson, S. Bhaduri and N.G. Connelly, *J. Organometal. Chem.*, 40 (1972) C36.
2 B.F.G. Johnson and J.A. Segal, *J. Chem. Soc. Dalton Trans.*, (1973) 478.
3 B.F.G. Johnson and J.A. McCleverty, *Progr. Inorg. Chem.*, 7 (1966) 277.
4 N.G. Connelly, *Inorg. Chim. Acta Revs.*, 6 (1972) 47.
5 B.F.G. Johnson and J.A. Segal, *Chem. Commun.*, (1972) 1312.
6 J. Ashley-Smith, B.F.G. Johnson and J.A. Segal, *J. Organometal. Chem.*, 49 (1973) C38.
7 N.G. Connelly and L.F. Dahl, *Chem. Commun.*, (1970) 880.
8 N.G. Connelly and J.D. Davies, *J. Organometal. Chem.*, 38 (1972) 385.
9 D.N. Kursanov, V.N. Setkina, P.V. Petrovskii, V.I. Zdanovich, N.K. Baranetskaya and J.D. Rubin, *J. Organometal. Chem.*, 37 (1972) 339.
10 B.V. Lokshin, V.I. Zdanovich, N.K. Baranetskaya, V.N. Setkina and D.N. Kursanov, *J. Organometal. Chem.*, 37 (1972) 331.
11 M.R. Churchill, *Chem. Commun.*, (1967) 777.
12 I.U. Khand, P.L. Pauson and W.E. Watts, *J. Chem. Soc. (C)*, (1969) 2024.
13 E.W. Abel and F.G.A. Stone, *Quart. Rev.*, 24 (1970) 516.