The Role of *C*-Chlorocarbenemetal Complexes in Carbene– and Carbyne–Metal Complex Chemistry; Experiments with $[Cr(CO)_5\{C(Cl)NMe_2\}]$ and $[Cr(CO)_5(\equiv CNMe_2)]^+$

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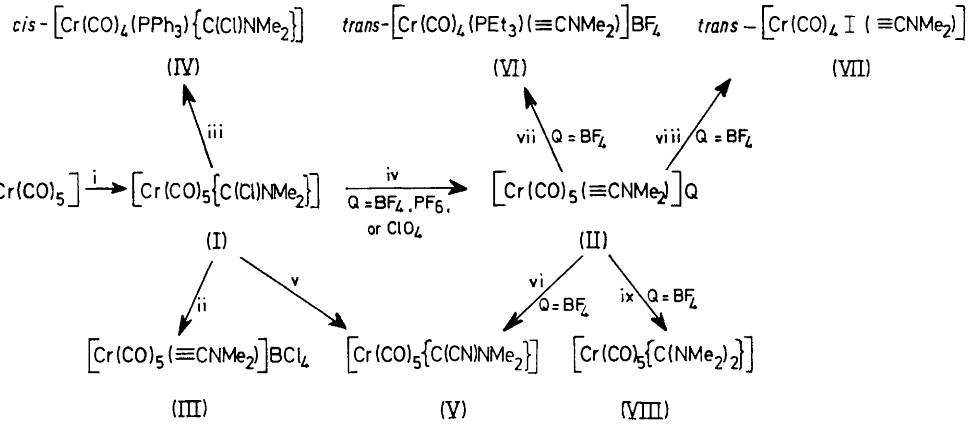
Summary Low temperature reaction of $[Cr(CO)_5\{C(Cl)NMe_2\}]$, (I), with (a) AgQ yields $[Cr(CO)_5(\equiv CNMe_2]^+Q^-$ ($Q = BF_4$, PF_6, or ClO_4), (II), (b) BCl_3 gives (II, $Q = BCl_4$), (c) PPh_3 affords *cis*-$[Cr(CO)_4(PPh_3)\{C(Cl)NMe_2\}]$, and (d) KCN gives $[Cr(CO)_5\{C(CN)NMe_2\}]$; the latter is also obtained from (II, $Q = BF_4$), which additionally with $LiNMe_2$ furnishes $[Cr(CO)_5\{C(NMe_2)_2\}]$ and with PEt_3 or $[Bu_4N]^+I^-$ the carbyne complexes *trans*-$[Cr(CO)_4(PEt_3)(\equiv CNMe_2)]^+[BF_4]^-$ or *trans*-$[Cr(CO)_4I(\equiv CNMe_2)]$.

RECENTLY we described some *C*-chlorocarbenemetal complexes, including $[Cr(CO)_5\{C(Cl)NMe_2\}]$,[1] (I), of interest in part because of their possible role as intermediates[1,2] in Fischer's carbynemetal synthesis. The latter employs a *C*-alkoxycarbenemetal precursor and a boron or related halide.[3] This communication focuses on compound (I) in order to illustrate further the significance of *C*-chlorocarbenemetal derivatives in this area of chemistry (see Scheme).

We now report (i) a new route to carbynemetal complexes from a *C*-chlorocarbene complex and Ag^+, (ii) a carbyne-metal-containing cation (II), showing for the first time no stabilising groups *trans*- to the carbyne species, (iii) a carbynemetal tetrachloroborate (III), obtained from (I) and BCl_3 and hence a further likely intermediate in the Fischer synthesis, (iv) some reactions of the *C*-chlorocarbenemetal complex (I) with nucleophiles, yielding to displacement of either CO to give (IV), or Cl^- from the liganded $-C(Cl)NMe_2$ to give the first *C*-cyanocarbenemetal complex, (V), and (v) some reactions of the cationic carbynemetal complex (II) with nucleophiles leading to loss of CO and formation of the *trans*-substitution product, (VI) or (VII), or to new *C*-functionalised carbenemetal complexes (V) and (VIII) {also prepared independently from $Na_2[Cr(CO)_5]$ and $[(Me_2N)_2CCl]Cl$}.[4]



SCHEME. i, $[Me_2NCCl_2]Cl$, ref. 1; ii, BCl_3, PhMe, −20 °C; iii, PPh_3, $h\nu$, −10 °C; iv, (a) AgQ,PhMe, −30°C, (b) Me_2CO; v, KCN,Me_2CO; vi, KCN, Me_2CO, −10 °C; vii, PEt_3, $h\nu$, −10 °C, Me_2CO; viii, $[Bu_4N]^+ I^-$, Me_2CO, −10 °C; ix, $LiNMe_2$, $HNMe_2$. (II): ν 2158m, 2110w, and 2033s (CO), 1050s br (BF_4), 840s br (PF_6), and 1040s br (ClO_4) cm^{-1}; τ $[(CD_3)_2CO]$ 6·37. (III): ν 2145m, 2120w, and 2045s (CO), and 660s br (BCl_4) cm^{-1}. (IV): ν (PhMe) 2044m, 1986m, 1931s, and 1884m (CO) cm^{-1}; τ ($CDCl_3$) 2·60 (m), 7·36 (s), and 7·46(s). (V): ν (hexane) 2066w, 1963m, and 1949s (CO) cm^{-1}, and ν (paraffin mull) 2192w (CN) cm^{-1}; τ (C_6D_6) 6·97 (s) and 7·47 (s). (VI): ν (CH_2Cl_2) 2090w, 2008sh, and 1989s (CO) cm^{-1}, and ν (paraffin mull) 1050s br (BF_4) cm^{-1}; τ $[(CD_3)_2CO]$ 6·53 (s, NMe_2), 7·95 (m, PCH_2Me obscured), and 8·75 (m, PCH_2Me). (VII): ν (CH_2Cl_2) 2093w, 2023sh, and 1996s (CO) cm^{-1}; τ (C_6D_6) 7·90 (s). (VIII): ν (C_6H_6) 2052w and 1920vs (CO) cm^{-1}; τ (C_6D_6) 7·53 (s).

The carbynechromium cationic complexes (II) were obtained in high yields (*ca.* 80%). The tetrafluoroborate and hexafluorophosphate are soluble in acetone and stable in this solvent for at least 5 h at −30 °C, and can be stored as solids at this temperature indefinitely. Decomposition in solution at higher temperature is rapid; $t_{\frac{1}{2}} = ca.$ 2 min at +30 °C from ^1H n.m.r. spectra in $(CD_3)_2CO$.

Compounds (II) and (IV)—(VIII) gave satisfactory analytical and spectroscopic data. Compound (III) was insufficiently stable for analysis and was identified by the similarity of the i.r. spectrum to that of (II) and strong absorption at *ca.* 660 cm^{-1} appropriate for $[BCl_4]^-$. ^1H n.m.r. spectra conveniently distinguish carbene– from carbyne–metal complexes, especially from respectively the nonequivalence or equivalence of the NMe_2 protons.

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[1] A. J. Hartshorn, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1975, 929.

[2] E. O. Fischer, W. Kleine, and F. R. Kreissl, *J. Organometallic Chem.*, 1976, **107**, C23.

[3] *Cf.* E. O. Fischer, *Adv. Organometallic Chem.*, 1976, **14**, 1, and references therein.

[4] B. Çetinkaya, unpublished results.