Journal of Organometallic Chemistry, 194 (1980) C57—C59
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Preliminary communication

REDUCTION-OXIDATION PROPERTIES OF ORGANOTRANSITION-METAL COMPLEXES

XI*. OXIDATION vs. CARBON—CARBON BOND FORMATION IN THE REACTIONS OF TETRACYANOETHYLENE WITH ELECTRON-RICH ORGANOMETALLIC CARBONYLS

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(Received May 19th, 1980)

Summary

With tetracyanoethylene the electron-rich complexes $[Cr(CO)_2L(\eta^6\text{-}C_6Me_6)]$ (I), $[Ru(CO)_2L(\eta^4\text{-}2,3\text{-}(CH_3)_2C_4H_4)]$ (II) and $[Fe(CO)_{3\text{-}n}L_n(\eta^4\text{-}COT)]$ (III, n = 1 or 2), (L = P-donor) undergo one-electron oxidation, Ru—C bond insertion, and 1,3-cyclo-addition, respectively.

The electrophile tetracyanoethylene (tcne) may either act as a one-electron oxidant towards organotransition-metal complexes [2] or undergo a variety [3] of other reactions including metal—carbon bond insertion [4] and cyclo-addition to coordinated polyolefins [5]. In order to define the factors which determine whether oxidation or an alternative is preferred we have investigated the reactions of tcne with the electron-rich complexes $[Cr(CO)_2L(\eta^6\text{-}C_6Me_6)]$ (I), $[Ru(CO)_2L(\eta^4\text{-}2,3\text{-}(CH_3)_2C_4H_4)]$ (II, $2,3\text{-}(CH_3)_2C_4H_4$ = 2,3-dimethylbuta-1,3-diene) and $[Fe(CO)_{3\text{-}n}L_n(\eta^4\text{-}COT)]$ (III, COD = cyclooctatetraene, n = 1 or 2); (L = P-donor) and with the parent tricarbonyls (I—III, L = CO). Preliminary results reveal that carbonyl substitution not only facilitates one-electron oxidation but also activates the substrate towards electrophilic attack both at the metal centre and at the coordinated organic ligand.

In CH_2Cl_2 (I, L = $P(OMe)_3$ or PPh_2Me) and tcne rapidly afford a deep green solution from which copper-like crystals of $[Cr(CO)_2(tcne)(\eta^6\text{-}C_6Me_6)]$ (IV, Table 1) may be isolated. By contrast (I, L = CO) and tcne yield a 1/1 charge-transfer adduct [6]. A comparison of the redox potentials** for the one-electron

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*For part X see ref. 1.

**All potentials are relative to a calomel electrode 1 M in LiCl and are measured at a platinum wire in CH_2Cl_2, 0.1 M in $[Et_4N][ClO_4]$. E_p is the oxidation potential for a reversible one-electron transfer; $(E_p)_{ox}$ is the peak potential for an irreversible one-electron oxidation measured by cyclic voltammetry at a scan rate of 100 mV sec^{-1}.

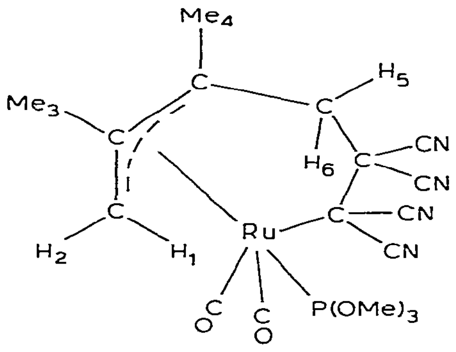

Fig. 1. Complex V.

TABLE 1

Complex	IR data (cm^{-1})[a]		^1H NMR data (τ)
	$\bar{\nu}$(CO)	$\bar{\nu}$(CN)	
IV	1 964s, 1 902s	2 217w, 2 197s	
V	2 054s, 2 005s	2 213w	[b]6.24 {d, J(PH) 12 Hz, $P(OMe)_3$}, 6.57 (dd, J(H(1)H(2)) 4 Hz, J(PH) 4 Hz, H(2)), 7.36 (dd, J(H(1)H(2)) 4 Hz, J(PH) 6 Hz, H(1)), 7.45 (d, J(H(5)H(6)) 14 Hz, H(5)), 7.89 (d, J(PH) 4 Hz, Me(3)), 7.92 (s, Me(4)), 8.30 (d, J(H(5)H(6)) 14 Hz, H(6))
VI ($n = 1$)	2 013s, 1 961s	2 242vw	[c]8.20 (m, H(10)), 6.44 {d, J(PH) 11 Hz, $P(OMe)_3$}, 6.30 (m, H(1)), 4.32 (m, H(2)), 3.48 (m, H(3)), 6.0—5.2 (m, H(4—7))

[a] In CH_2Cl_2; vw = very weak, w = weak, s = strong. [b] In $CDCl_3$, numbering as in Fig. 1. [c] In CD_2Cl_2, numbering as in Fig. 2.

oxidation of I (L = CO, E_p = 0.55 V [7], L = $P(OMe)_3$, E_p = 0.08 V [8]; L = PPh_2Me, E_p = −0.08 V) with that for the one-electron reduction of tcne (E_p = 0.16 V) clearly shows that IV is formed via displacement of L from $[Cr(CO)_2L(\eta^6\text{-}C_6Me_6)]^+$ by $[tcne]^-$; similar oxidative-substitution cannot occur for I (L = CO).

Although tcne cannot oxidise even the most electron-rich example of II (L = PPh_3, $(E_p)_{ox}$ = 0.70 V) Ru—C bond insertion is facilitated by phosphine substitution. Thus, II (L = CO) does not react with tcne but II (L = PPh_3 or $P(OMe)_3$) are rapidly and quantitatively converted to pale yellow V (Fig. 1, Table 1) at room temperature.

Substitution of the carbonyl ligands of III (n = 0) leads to drastic lowering of the potential at which oxidation occurs III (n = 0, $(E_p)_{ox}$ = 0.88 V; n = 1; L = $P(OMe)_3$, $(E_p)_{ox}$ = 0.48 V; n = 2, L = $P(OMe)_3$, $(E_p)_{ox}$ = 0.12 V). Although one-electron oxidation of III (n = 2, L = $P(OMe)_3$) is possible, 1,3-cycloaddition of tcne occurs to give pale yellow VI (n = 1 or 2, Fig. 2, Table 1), entirely analogous to the product [5] from III (n = 0). However, only the bis-phosphite complex VI (n = 2) undergoes thermolysis, in refluxing tetrahydrofuran, to an as yet incompletely characterised red complex (ν(CO) 1 981s cm^{-1}, ν(CN) 2 177s cm^{-1}, (in CH_2Cl_2)). Studies on this species, and on further aspects of the activation of organometallic carbonyls towards electrophilic reagents are in progress.

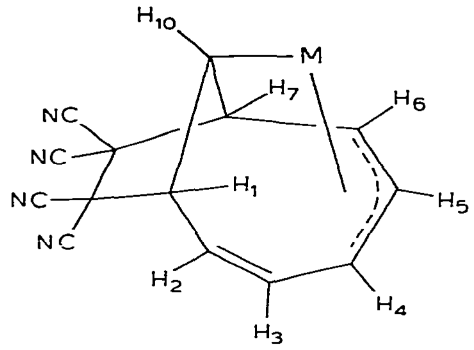

Fig. 2. Complex VI, M = $Fe(CO)_{3-n}\{P(OMe)_3\}_n$.

Acknowledgement

We thank Johnson-Matthey for a generous loan of ruthenium trichloride.

References

1 N.G. Connelly, R.L. Kelly, and M.W. Whiteley, J. Chem. Soc., in press.
2 J.W. Fitch and J.J. Lagowski, Inorg. Chem., 4 (1965) 864.
3 W.H. Baddley, Inorg. Chim. Acta Revs., 2 (1968) 7.
4 J.A. Hanna and A. Wojcicki, Inorg. Chim. Acta, 9 (1974) 55.
5 M. Green, S. Heathcock, and D.C. Wood, J. Chem. Soc. Dalton, (1973) 1564.
6 P.G. Sennikov, V.A. Kuznetsov, A.N. Egorochkin, N.I. Sirotkin, R.G. Nazarova, and G.A. Razuvaev, J. Organometal. Chem., 190 (1980) 167.
7 M.L. Lloyd, J.A. McCleverty, J.A. Connor, and E.M. Jones, J. Chem. Soc. Dalton, (1973) 1768.
8 N.G. Connelly, Z. Demidowicz, and R.L. Kelly, J. Chem. Soc. Dalton, (1975) 2335.