

Preliminary communication

REACTIONS BETWEEN TETRACYANOETHYLENE AND TRANSITION METAL ACETYLIDES: FORMATION AND CLEAVAGE OF THE CYCLOBUTENYL RING IN AN AUTHENTIC TETRACYANOCYCLOBUTENYL-METAL COMPLEX, $W[\bar{C}=\text{CPhC}(\text{CN})_2\bar{C}(\text{CN})_2](\text{CO})_3(\eta\text{-C}_5\text{H}_5)$

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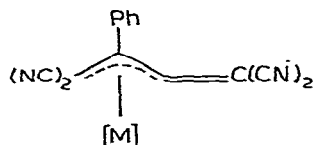
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Summary

The reaction between $W(\text{C}\equiv\text{CPh})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ and $\text{C}_2(\text{CN})_4$ affords $W[\bar{C}=\text{CPhC}(\text{CN})_2\bar{C}(\text{CN})_2](\text{CO})_3(\eta\text{-C}_5\text{H}_5)$, which has been characterised by X-ray crystallography; the four-membered ring is cleaved thermally to give $W[\text{C}\{\text{=C}(\text{CN})_2\}\text{CPh}=\text{C}(\text{CN})_2](\text{CO})_3(\eta\text{-C}_5\text{H}_5)$, which in turn is converted photochemically to $W[\eta^3\text{-C}(\text{CN})_2\text{CPhC}\{\text{=C}(\text{CN})_2\}](\text{CO})_2(\eta\text{-C}_5\text{H}_5)$.

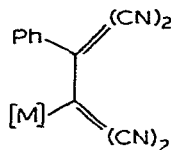
We have previously reported the reactions between $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)(\text{L})$ ($\eta\text{-C}_5\text{H}_5$) and tetracyanoethylene which afford allylic (Ia, $\text{L} = \text{PPh}_3$) or butadienyl complexes (IIa, $\text{L} = \text{CO}$) [1]. These reactions proceed via deeply coloured paramagnetic intermediates, which are slowly converted to the isolated complexes; we have postulated the intermediacy of a tetracyanocyclobutenyl complex (IIIa), but this was not isolated. We now describe the isolation and structural characterisation of an authentic cyclobutenyl complex, and its stepwise conversion into butadienyl and allylic complexes related to I and II.

Tetracyanoethylene reacts immediately with $W(\text{C}\equiv\text{CPh})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ in dichloromethane to give a greenish-brown paramagnetic intermediate ($g = 1.997$, C_6H_6). After 90 min work-up and crystallisation from ethanol afforded yellow $W[\bar{C}=\text{CPhC}(\text{CN})_2\bar{C}(\text{CN})_2](\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ (IIIb) in 76% yield ($\nu(\text{CN})$ 2244w, $\nu(\text{CO})$ 2046s, 1983vs, 1974(sh) cm^{-1} ; ^1H NMR: δ [$(\text{CD}_3)_2\text{CO}$] (ppm) 6.16s (C_5H_5), 7.64s(br) (Ph); ^{13}C NMR: δ [$(\text{CD}_3)_2\text{CO}$] (ppm) 94.0s (C_5H_5), 112.2s, 113.2s (CN), 127.1–131.7m (Ph), 216.7s (CO)). Full confirmation of the nature of complex IIIb was obtained by a single-crystal X-ray structure.



(Ia . [M] = Ru(PPh₃)(η-C₅H₅) ;

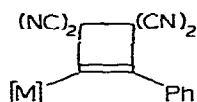
Ib . [M] = W(CO)₂(η-C₅H₅))



(IIa . [M] = Ru(L)(PPh₃)(η-C₅H₅) ;

IIb . [M] = W(CO)₃(η-C₅H₅) ;

IIc . [M] = Fe(CO)₂(η-C₅H₅))



(IIIa . [M] = Ru(PPh₃)(L)(η-C₅H₅) ;

IIIb . [M] = W(CO)₃(η-C₅H₅) ;

IIIc . [M] = Fe(CO)₂(η-C₅H₅))

Crystal data. C₂₂H₁₀N₄O₃W, F.W. = 562.2; triclinic, space group $P\bar{1}$, a 9.000(3), b 10.590(3), c 11.432(4) Å, α 76.53(3), β 70.77(3), γ 88.31(3)°; U 999.2 Å³; Z = 2, D_c 1.868, D_m 1.85(2) g cm⁻³. $F(000)$ 536 electrons, $\mu(\text{Mo-K}\alpha)$ 59.37 cm⁻¹.

The yellow platy crystals decompose rapidly in light, and were coated with colloidal graphite for data collection. The structure was solved by normal heavy-atom techniques; block-matrix least-squares techniques were employed for refinement of all positional and thermal (anisotropic for non-hydrogen atoms) parameters. Hydrogen atoms were included at calculated sites (C—H 0.95 Å) with two separate group temperature factors. The SHELX system of programmes was used for all calculations. Of the 3663 reflections collected ($1.5^\circ \leq \theta \leq 25^\circ$), 2786 with $I > 2.5\sigma(I)$ were used, to give final values of R and R_w of 3.61 and 3.84%, respectively, with $w = 1.16 (\sigma^2 F_o + 0.001 F_o^2)$.

Figure 1 shows the molecular structure of IIIb; important bond parameters are collected in Table 1. Of most interest is the cyclobutenyl group which has nearly perfect planarity, and is σ -bonded to tungsten via one of the olefinic carbon atoms. The C(12)—C(15) bond is unusually long (1.60(1) Å), with acute intra-ring angles of 83.6(6) and 86.7(6)° at C(12) and C(15), respectively. Other bond distances involving the ring carbons are normal, and these exceptional features are entirely consistent with the ready cleavage of the C(12)—C(15) bond described below.

In solution at ambient temperature, not all the ¹³C resonances of IIIb could be recorded before conversion to a second, isomeric complex was complete. Orange crystals of this complex, identified as the butadienyl derivative I Ib, were also obtained in 68% yield from a reaction between C₂(CN)₄ and W(C≡CPh)(CO)₃(η-C₅H₅) carried out in the dark for 2 d. (M^+ at m/e 562 (for ¹⁸⁴W); $\nu(\text{CN})$ 2222m, 2210m, $\nu(\text{CO})$ 2046s, 1981vs(br), $\nu(\text{C}=\text{C})$ 1522s cm⁻¹; ¹H NMR: δ [(CD₃)₂CO] 5.91s (C₅H₅), 7.8m (Ph); ¹³C NMR: δ [(CD₃)₂CO] 77.4s, 99.8s, 182.8s, 221.8s (carbons of C=C—C=C chain), 95.7s (C₅H₅),

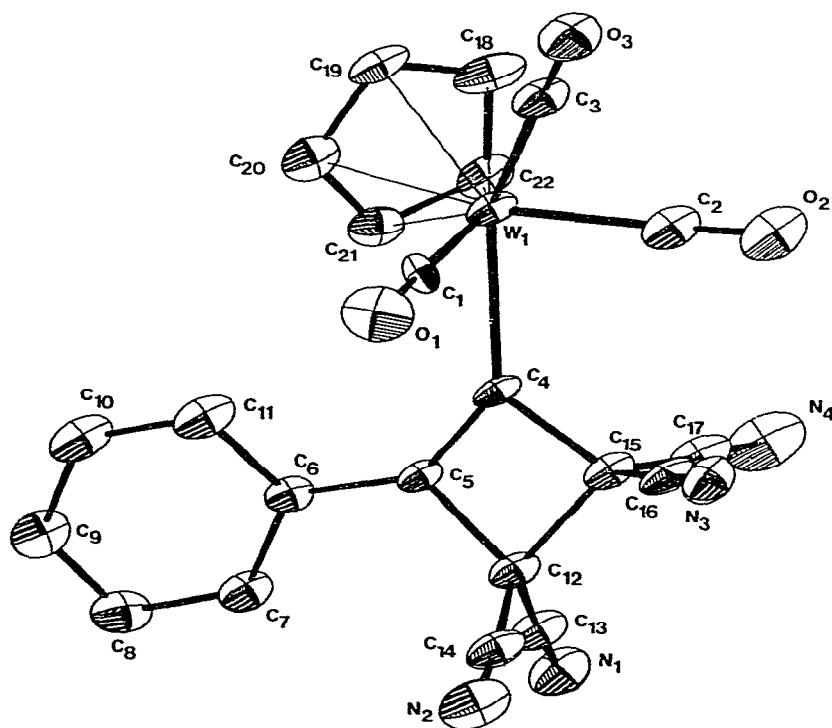


Fig. 1. An ORTEP plot of the molecular structure of $W[C\equiv CPhC(CN)_2C(CN)_2](CO)_3(\eta-C_5H_5)$ (IIIb).

TABLE 1

IMPORTANT BOND LENGTHS (Å) AND ANGLES (°) FOR IIIb

Bond lengths (Å)		Bond angles (°)	
W(1)—C(1)	1.987(9)	W(1)—C(4)—C(5)	138.9(6)
W(1)—C(2)	1.981(8)	W(1)—C(4)—C(15)	129.3(5)
W(1)—C(3)	2.004(10)	C(5)—C(4)—C(15)	91.8(7)
W(1)—C(4)	2.202(9)		
		C(4)—C(5)—C(6)	137.4(8)
W(1)—C(18)	2.302(9)	C(4)—C(5)—C(12)	97.9(6)
W(1)—C(19)	2.307(11)	C(6)—C(5)—C(12)	124.6(8)
W(1)—C(20)	2.332(9)		
W(1)—C(21)	2.311(8)	C(5)—C(12)—C(13)	117.9(6)
W(1)—C(22)	2.299(8)	C(5)—C(12)—C(14)	113.0(6)
		C(5)—C(12)—C(15)	83.6(6)
C(4)—C(5)	1.344(11)	C(13)—C(12)—C(14)	110.7(9)
C(4)—C(15)	1.552(11)	C(13)—C(12)—C(15)	113.2(6)
C(5)—C(12)	1.524(12)	C(14)—C(12)—C(15)	116.1(6)
C(12)—C(15)	1.602(13)		
C(5)—C(6)	1.468(10)	C(4)—C(15)—C(12)	86.7(6)
		C(4)—C(15)—C(16)	114.5(6)
C(12)—C(13)	1.479(11)	C(4)—C(15)—C(17)	115.0(7)
C(12)—C(14)	1.474(13)	C(12)—C(15)—C(16)	113.2(7)
C(15)—C(16)	1.463(10)	C(12)—C(15)—C(17)	113.4(7)
C(15)—C(17)	1.463(11)	C(16)—C(15)—C(17)	111.9(7)

113.0s, 113.3s, 113.5s, 116.2s (CN), 129.8–134.9m (Ph), 196.9s, 216.8s, 217.8s (CO)). The mother liquor afforded a few crystals of a third complex, which was later obtained in 62% yield by UV irradiation of IIb in acetone for 25 h. This complex was characterised as the allylic complex Ib (M^+ at m/e 534 (for ^{184}W); $\nu(\text{CN})$ 2232s, 2222m, $\nu(\text{CO})$ 2080vs, 2025vs, $\nu(\text{CC})$ 1586s cm^{-1} ; ^1H NMR: $\delta(\text{CDCl}_3)$ 5.89s (C_5H_5), 7.5m (Ph); ^{13}C NMR: $\delta(\text{CDCl}_3)$ 4.7s, 79.4s, 201.1s, 203.8s ($\text{C}\equiv\text{C}\equiv\text{C}=\text{C}$ chain), 94.1s (C_5H_5), 112.2s, 115.2s, 116.5s, 118.4s (CN), 128.7–131.5m (Ph), 206.6s (CO)) by a single-crystal structural study, to be reported elsewhere, which also revealed a molecule of tetracyanoethylene in the unit cell.

These experiments thus confirm the (2+2) cycloaddition of tetracyanoethylene to a transition metal acetylide, and further demonstrate the ready transformation of the adduct into η^1 -butadienyl and η^3 -allyl complexes, analogous to those described earlier for ruthenium [1]. These reactions occur under extremely mild conditions.

Related cyclobutenyliron complexes have been described from similar reactions between tetracyanoethylene and $\text{Fe}(\text{C}\equiv\text{CPh})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [2]. In our hands, qualitatively similar reactions proceeded via a green paramagnetic intermediate ($g = 1.997$, C_6H_6) which rapidly forms a yellow complex; this the previously described "dipolar intermediate", and is probably the cyclobutenyl complex IIIc. Ring-opening affords the second orange complex (Davison and Solar's cyclobutenyl derivative) which on the basis of its spectroscopic properties, would appear to be the butadienyl complex IIc ($\nu(\text{CN})$ 2220m, 2207m, 2201m, $\nu(\text{CO})$ 2054s, 2009s, $\nu(\text{CC})$ 1533m, 1528(sh) cm^{-1} ; ^1H NMR: $\delta(\text{CDCl}_3)$ 4.93s (C_5H_5), 7.60m (Ph); ^{13}C NMR: $\delta(\text{CDCl}_3)$ 74.9s, 98.0s, 181.2s, 215.1s (carbons of butadiene chain), 86.9s (C_5H_5), 110.6, 112.5, 115.8 (all s, CN), 128.5–133.7m (Ph), 209.3s, 211.0s (CO); cf. data for IIb above).

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