Novel 2-Aza-allylidene Complexes: Synthesis and *X*-Ray Structure of *trans*-Br(CO)$_4$W[CNCPh$_2$]

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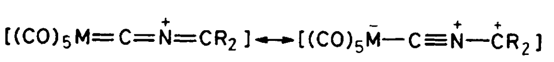
The replacement of the *trans*-CO group by Br$^-$ in cationic [(CO)$_5$W=C=N=CR$_2$]AlBr$_4$ complexes causes a drastic change in the geometry of the CNCR$_2$ ligand; the molecular structure of the phenyl-substituted product, *trans*-Br(CO)$_4$W[CNCPh$_2$], is established by single crystal *X*-ray diffraction.

Electronic effects and electron delocalization within transition metal complexes have attracted much interest since understanding the relationship between electron delocalization and structure and reactivity of co-ordinated groups is crucial for the evaluation of possible elementary reaction steps in catalytic processes and biological systems. Recently we prepared 2-aza-allenylidene complexes, [(CO)$_5$M=C=N=CR$_2$]$^+$BF$_4^-$ [R = aryl; (**1**)BF$_4$ M = Cr, (**2**)BF$_4$ M = W], containing a new type of heterocumulenic ligand, [=C=N=CR$_2$]$^+$,[1] which is formally derived from allenylidene (propadienylidene) ligands[2] by isoelectronic substitution of N$^+$ for C. The CNC fragment in these complexes is

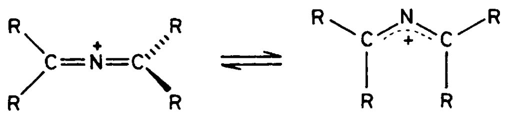
$$[(CO)_5M{=}C{=}N{=}CR_2]^+BF_4^-$$

(**1**) M = Cr

(**2**) M = W



(A) (B)



(C) (D)

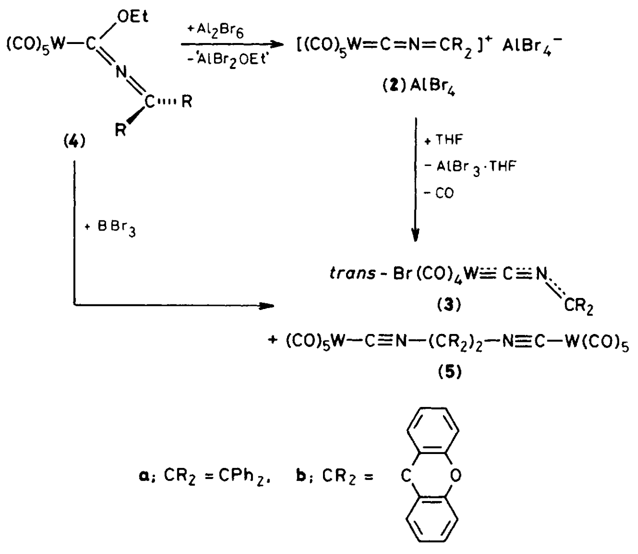
almost linear [$(\mathbf{1})BF_4$ $CR_2 = C(C_6H_4)_2O$, C–N–C angle 171°].[1] They exhibit unusual photochemical properties and are best formulated as hybrids of the resonance structures (A) and (B).

We now report the synthesis of novel *trans*-$Br(CO)_4W[CNCR_2]$ complexes (**3**). In contrast to (**1**)BF_4 and (**2**)BF_4, the C–N–C fragment in (**3**) is strongly bent and the MC–N distance is significantly enlarged. Therefore, the compounds (**3**) constitute the first examples of 2-aza-allylidene complexes containing a ligand which is derived from the 2-aza-allyl isomeric form (D) of $[R_2CNCR_2]^+$ by displacement of R_2 by a metal carbonyl fragment.

When $[(CO)_5W{=}C{=}N{=}CPh_2]AlBr_4$, (**2a**)$AlBr_4$, prepared from $(CO)_5W[C(OEt)N{=}CPh_2]$,[3] (**4a**), and Al_2Br_6 in CH_2Cl_2 at −10 °C,[1] was treated in CH_2Cl_2 at −40 °C with an excess of freshly distilled (over $LiAlH_4$) tetrahydrofuran (THF), the original deep blue solution immediately turned red and *trans*-$Br(CO)_4W[CNCPh_2]$, (**3a**), as well as small amounts of the dinuclear bis(isonitrile) complex (**5a**) (Scheme 1) were formed. Purification by column chromatography [SiO_2, pentane–CH_2Cl_2 (1 : 1)] followed by recrystallization from Et_2O gave dark-red crystals of (**3a**) (67% yield). However, when (**4a**) was treated at ambient temperature with BBr_3 [(**4a**) : BBr_3 = 1 : 1.2] instead of Al_2Br_6, the main product was (**5a**) (isolated: 44%) which corresponds to the product of a reductive coupling of two (**2a**) moieties. In this case, (**3a**) was only formed in minor amounts.

In analogy to the preparation of (**3a**) from (**2a**)$AlBr_4$ and THF, (**3b**) was obtained from (**2b**)$AlBr_4$ and THF (isolated: 15%). The compounds (**3a**), (**3b**), and (**5a**) were characterized by elemental analysis and by spectroscopic means.† The structure of (**3a**) was also determined by an *X*-ray analysis (Figure 1).‡ In contrast to (**1b**)BF_4, the C–N–C fragment strongly deviates from linearity [C–N–C angle 135.4° in (**3a**), 171.0° in (**1b**)[1]]. The N–C-6 distance is similar to those normally found in *bent* 2-aza-allyl cations [(D): 132—134 pm [4] *vs*. 127—128 pm in 2-aza-allenium cations (C)[5,6]]. The C-5–N distance is somewhat shorter and resembles those recently observed for almost linear 2-aza-allenium cations.[5,6] However, the smaller C-5–N bond length in (**3a**) is probably due to the sp hybridization of C-5. The W–C-5 distance is very short, comparable to that found in the carbyne complex *trans*-$Br(CO)_4W{\equiv}CMe$ [182(4) pm].[7]

The complexes (**3a**) and (**3b**) are dark-red and violet, respectively. The low-energy absorptions can be assigned to metal-to-ligand charge transfer transitions. In sharp contrast to the cations (**2**), these transitions shift toward lower energies with increasing ability of the substituent R to π-donate electron density into the CNC fragment [$CR_2 = CPh_2$,



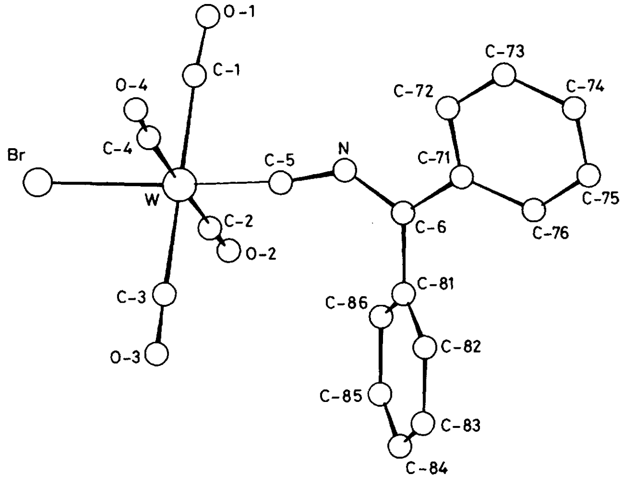


Figure 1. Molecular structure of *trans*-$Br(CO)_4W[CNCPh_2]$, (**3a**). Some important distances (pm) and angles (°) are (e.s.d.s. in parenthesis): W–C-5 187.8(5), C-5–N 127.5(7), N–C-6 132.4(7), W–Br 264.4(1); W–C-5–N 169.6(5), C-5–N–C-6 135.4(5); angle between plane 1 (Br,W,C-1,C-3,C-5) and plane 2 (C-5,N,C-6): 26.1°, between plane 3 (N,C-6,C-71,C-81) and the planes of the phenyl rings: 19.2° and 42.8°, respectively.

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† *Selected spectroscopic data*. (**3a**): I.r. ν_{CO} (hexane) 2105m, 2019s; ν_{CNC} (KBr) 1540s cm^{-1}; ^{13}C n.m.r. (CD_3COCD_3, −20 °C, relative to CD_3COCD_3) δ 197.8 (C-5), 192.2 (CO), 172.0 (C-6); u.v.–visible (hexane) $\lambda_{max.}$ 482 (log ε 3.9), 465 (3.9), 285 nm (4.4). (**3b**): i.r. ν_{CO} (CH_2Cl_2) 2093m, 1999s, 1985m cm^{-1}; ν_{CNC} (KBr) 1575s cm^{-1}; u.v.–visible (1,1,2-trichloroethane) $\lambda_{max.}$ 595sh., 548 (log ε 4.1), 510 sh. nm. (**5a**): i.r. ν_{CO} (hexane) 2053m, 1960vs; ν_{CN} 2142w cm^{-1}.

‡ *Crystal data* for (**3a**): $C_{18}H_{10}BrNO_4W$, triclinic, space group $P\bar{1}$, a = 939.6(2), b = 956.5(2), c = 1188.0(3) pm, α = 112.28(2), β = 109.89(2), γ = 89.13(2)°, $U = 921 \times 10^{-6}$ pm^3, Z = 2, D_c = 2.05 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 89.5 cm^{-1}, empirical absorption correction; graphite-monochromated Mo-K_α-radiation, ω-scan, $2\theta_{max.}$ 52°. 3630 Independent reflexions were measured at −40 °C. The structure was solved by the heavy atom method (W, Br from a Patterson-, other non-H atoms from a difference Fourier-synthesis) and refined by full-matrix least-squares (226 parameters, 3351 structural factors [$F_0 > 3.926\ \sigma\ F_0$], H-atoms included but fixed). Final R 0.027, R_w 0.030. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$C(C_6H_4Br\text{-}p)_2$, $C(C_6H_4OMe\text{-}p)_2$, $C(C_6H_4)_2O$]. Generally, the reverse is true for (**2**).

These results demonstrate that by substitution of the weak π-donor Br^- for the strong π-acceptor group CO in the metal–carbonyl fragment a drastic change in the geometry and the electronic properties of the $CNCR_2$ ligand can be achieved. In agreement with these observations are the results of *X*-ray analyses and quantum mechanical calculations obtained with different $[R_2C{=}N{=}CR_2]^+$ cations:[6] increasing ability of R to donate electron density stabilizes form (D) relative to (C). Thus, whereas $[H_2C{=}N{=}CH_2]^+$ should be linear, the diaminosubstituted cation $[(Me_2N)HCNCH(NMe_2)]^+$ adopts the bent structure (D).

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