The Preparation and Characterisation of New Mixed Carbonyl Nitro Complexes of Group 6 Metals

Anke Sieker, Alexander J. Blake, Simon Parsons and Brian F. G. Johnson *
Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

The series of carbonyl nitro monoanions $[M(CO)_5(NO_2)]^-$ (M = Cr, Mo or W) has been isolated as their $N(PPh_3)_2^+$ salts from the reaction of the parent hexacarbonyl, $M(CO)_6$, with Me_3NO in CH_2Cl_2 in the presence of $[N(PPh_3)_2][NO_2]$ and has been fully characterised in solution by IR spectroscopy and by single-crystal X-ray diffraction studies in the solid for M = Cr or W as the PPh_4^+ salt.

The ability of transition-metal ions to catalyse the reduction of NO_x compounds to N_2O and ultimately to N_2 is of enormous fundamental and commercial importance, yet the reactions involved remain poorly understood. In earlier work we concentrated on the oxygen-atom-transfer reaction which occurred between NO and CO to produce N_2O and CO_2,[1] and on the reaction of metal nitrosyl derivatives with dioxygen to produce co-ordinated NO_2.[2] We hoped to establish an oxidation–reduction cycle based on the basic 'M–N' unit [equation (1)].

$$\{M(NO_2)\} \underset{+\frac{1}{2}O_2}{\overset{+CO}{\rightleftharpoons}} \{M(NO)\} \underset{+\frac{1}{2}O_2}{\overset{+CO}{\rightleftharpoons}} \{MN\} \qquad (1)$$

In this communication we report our extension of these studies to the sterically crowded species $[M(CO)_5(NO_2)]^-$ (M = Cr, Mo or W). The anion $[Cr(CO)_5(NO_2)]^-$ was first prepared by Mantell and Gladfelter[3] from the reaction between $[Cr(CO)_5(thf)]$ (thf = tetrahydrofuran) and $[N(PPh_3)_2][NO_2]$. Although the basic formula of the anion was established by the usual spectroscopic and analytical techniques, the species was not characterised structurally. However a nitro co-ordination was favoured on the basis of isotopic-enrichment (^{15}N) experiments. A surprising feature of the chemistry of this anion is the observation that it does not transform into the nitrosyl anion $[Cr(CO)_4(NO)]^-$ on heating. The direct reaction of $Cr(CO)_6$ with $[N(PPh_3)_2][NO_2]$ is known to produce this nitrosyl species and it was thought that the nitro anion $[Cr(CO)_5(NO_2)]^-$ would be a logical intermediate followed by intramolecular oxygen-atom transfer and CO_2 ejection.

We have now prepared salts of the monoanion $[Cr(CO)_5(NO_2)]^-$ and of the corresponding monoanions of both molybdenum and tungsten, and have established the molecular and crystallographic structures of both $[PPh_4][Cr(CO)_5(NO_2)]$ and $[PPh_4][W(CO)_5(NO_2)]$.

Reaction of $M(CO)_6$ (M = Mo or W) with $[N(PPh_3)_2][NO_2]$ in tetrahydrofuran at elevated temperatures produces the monoanion $[M(CO)_5(NO_2)]^-$ quantitatively, but the reaction is complicated by the further reaction of this anion to produce the more highly substituted mixed carbonyl nitro complex anion $[M(CO)_3(NO_2)_3]^{3-}$. We find that reaction of $M(CO)_6$ with Me_3NO in CH_2Cl_2 in the presence of RNO_2 [R = $N(PPh_3)_2^+$ or PPh_4^+] provides a better and more convenient route [equation (2)].

$$M(CO)_6 + Me_3NO + NO_2^- \longrightarrow [M(CO)_5(NO_2)]^- + NMe_3(g) + CO_2(g) \qquad (2)$$

In a typical reaction $M(CO)_6$ dissolved in CH_2Cl_2 was treated with 1 equivalent of RNO_2 and Me_3NO at −30 °C. An immediate change in the solution from colourless to yellow was detected and on warming the mixture to room temperature complete conversion to the required product was observed. This reaction is best monitored by IR spectroscopy when the single $\nu(CO)$ band of $M(CO)_6$ is replaced by the three diagnostic absorptions of the $[M(CO)_5(NO_2)]^-$ species [$\nu(CH_2Cl_2)/cm^{-1}$ 2066vw, 1931(br)vs and 1878m (in accordance with literature values[3]) for M = Cr; 2072vw, 1932(br)vs and 1873m for M = Mo; and 2067vw, 1924(br)vs and 1870m for M = W]. However, the co-ordination mode of the NO_2^- ligands had to be proven by X-ray analysis in the crystalline state.†

Attempts to form crystalline salts using $N(PPh_3)_2^+$ as counter ion were unsuccessful. We believe that this is a consequence of the unfavourable differences in size between cation and anion [$V_{N(PPh_3)_2^+} = 490\ \text{Å}^3$].[4] However, use of the smaller tetraphenylphosphonium cation ($V_{PPh_4^+} = 317\ \text{Å}^3$)[4] meant that two species of the triad could be crystallised in sufficient quality to undertake an X-ray structure investigation ‡ at low temperature (150 K). Thus, the isomorphous complexes $[PPh_4][Cr(CO)_5(NO_2)]$ **1** (pale lemon-yellow tablet) and $[PPh_4][W(CO)_5(NO_2)]$ **2** (yellow block) crystallise in the monoclinic space group *C*2/*c*. Upon structure solution the

---

† Due to the absence of comparable data and the simultaneous presence of the $N(PPh_3)_2^+$ or PPh_4^+ counter ion assignment of the NO_2^- vibrations in the IR spectrum is difficult in both the solution and solid state. One band is observed at 1303 cm^{-1} for M = Cr (in CH_2Cl_2) and for M = W a shoulder at *ca.* 1300 cm^{-1} (in CH_2Cl_2) is detected. The other vibration, believed to occur between 1200 and 1300 cm^{-1} is obscured by the solvent CH_2Cl_2.

‡ *Crystal data.* **1.** $C_{29}H_{20}CrNO_7P$, $M = 577.43$, monoclinic, space group *C*2/*c*, $a = 22.21(3)$, $b = 6.945(8)$, $c = 17.28(3)$ Å, $\beta = 98.80(12)°$, $U = 2634(7)$ Å^3 [from 2θ values of 8 setting reflections measured ($21 \leqslant 2\theta \leqslant 24°$)], $Z = 4$, $D_c = 1.456$ g cm^{-3}, $T = 150$ K, $\mu = 0.544$ mm^{-1}, $F(000) = 1184$, size 0.54 × 0.47 × 0.12 mm. **2.** $C_{29}H_{20}NO_7PW$, $M = 709.28$, monoclinic, space group *C*2/*c*, $a = 22.271(4)$ $b = 7.0498(11)$, $c = 17.277(3)$ Å, $\beta = 99.136(23)°$, $U = 2678(8)$ Å^3 [from 2θ values of 32 reflections measured at $\pm\omega(30 \leqslant 2\theta \leqslant 32°)$], $Z = 4$, $D_c = 1.759$ g cm^{-3}, $T = 150$ K, $\mu = 4.421$ mm^{-1}, $F(000) = 1384$, size 0.70 × 0.54 × 0.35 mm. Stoë-Stadi-4 four-circle diffractometer, graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), ω **1**, ω–θ **2** scans. All data were corrected for absorption. Both structures were solved by direct methods.[5] In both cases, all fully occupied non-hydrogen atoms were refined anisotropically and the NO_2 group and the CO group *trans* to it are scrambled such that each component has an occupancy factor of 0.5. In **2** the oxygen of one equatorial carbonyl ligand is disordered over two half-occupied positions. In both complexes the distances C(3)–O(3), N–O(1N), N–O(2N) and O(1N) ··· O(2N) were restrained to be 1.14, 1.25, 1.25 and 2.18 ± 0.02 Å respectively to allow satisfactory refinement. Also, Cr–C(3) and Cr ··· O(3) in **1** and W–C(3) in **2** were restrained to be 1.90, 3.04 and 2.03 ± 0.02 Å respectively. The final *R* factors are $R1 = 0.0742$ (for **1**) and 0.0309 (for **2**) for 902 and 1583 observed [$F > 4\sigma(F)$] data, respectively, and $wR2 = 0.2264$ (for **1**) and 0.0793 (for **2**) for all 1227 and 1761 independent reflections ($2\theta \leqslant 45°$), respectively. $w^{-1} = \sigma^2(F^2) + (0.1525P)^2 + 8.88P$ for **1**, $\sigma^2(F^2) + (0.0332P)^2 + 27.85P$ for **2**, where $P = [\max.\ (F_o^2, 0) + 2F_c^2]/3$. Both refinements used SHELX 93.[6] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

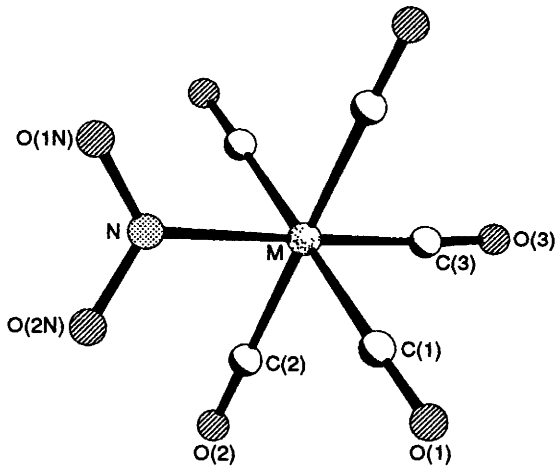

Fig. 1 Molecular structure of the anion in **1** and **2**. Selected bond distances (Å) for **1**: Cr–C(3) 1.890(8), Cr–C(2) 1.900(11), Cr–C(1) 1.906(12), Cr–N 2.13(2), C(1)–O(1) 1.151(11), C(2)–O(2) 1.125(10), C(3)–O(3) 1.127(9), N–O(1N) 1.243(10) and N–O(2N) 1.246(10). All angles of the anion are within ± 4° of the ideal values of 90 and 180° respectively, except for O(1N)–N–O(2N) 114(2), O(1N)–N–Cr 126.6(13) and O(2N)–N–Cr 119.3(13)°. Selected bond distances (Å) and angles (°) for **2**: W–C(1) 2.037(9), W–C(2) 2.018(8), W–C(3) 2.037(3), W–N 2.189(11), C(1)–O(1) 1.145(9), C(2)–O(2) 1.160(12), C(3)–O(3) 1.143(2), N–O(1N) 1.252(3) and N–O(2N) 1.249(3); C(1)–W–N 97.4(4), C(2)–W–N 84.7(5), C(2)–W–C(1) 89.6(3), C(2)–W–C(3) 95.5(4) and C(3)–W–C(1) 88.2(4)

anticipated formula was confirmed, as was the co-ordination mode of the NO_2^- ligand in the expected nitro form. The structure of the anions is shown in Fig. 1, together with bond distances and angles. During refinement some disorder was found in both anions. The central metal was shown to lie on an inversion centre, which means that the nitro ligand and the carbonyl group in the *trans* position to it must be scrambled. Refinement confirmed a 50% occupancy of the site by each component. The tungsten species showed additional disorder in one of its equatorial carbonyl groups, where the oxygen atom resides in two half-occupied positions.

As the first- and third-row member of this triad were found to co-ordinate the incoming NO_2^- in the nitro-bonding mode and the IR spectrum of $[Mo(CO)_5(NO_2)]^-$ is strikingly similar to both the chromium and tungsten species, it is thought that the NO_2^- in this case also co-ordinates *via* its nitrogen atom.

The preference of the nitro- over the nitrito-mode has already been observed in the related complexes of manganese and rhenium,[7] but so far no explanation for this behaviour could be found. The nitro mode is however generally thought to be more stable than co-ordination through an oxygen atom of an *O*NO group. Anticipated differences in NO_2^- co-ordination due to changes in the size of the central metal atom were however not observed, although the substitution reaction was slower for tungsten than for chromium. Intermediates such as linkage isomers of the NO_2^- ligand were not detected during the course of the reaction.

This new synthesis is favoured over the two-step approach pioneered for chromium by Mantell and Gladfelter,[3] and yields quantitative results for all three metals within this triad. The preparation of the tetrahydrofuran substituted intermediate can also be carried out *via* activation with Me_3NO, but in order to convert all $M(CO)_5(thf)$ into the nitro compound an excess of $[N(PPh_3)_2][NO_2]$ or $[PPh_4][NO_2]$ was necessary.

The isolation and characterisation of these mixed carbonyl nitro complexes gives further insight into the phenomenon of oxygen-atom transfer, as it shows that nitro co-ordination is stable in the presence of CO and might therefore not participate in the relocation of one of its oxygen atoms to an adjacent carbon, with a consequent loss of CO_2. The observed stability is also in sharp contrast to earlier assumptions that these complexes are undergoing spontaneous reductions *via* oxygen-atom transfer. This hypothesis, which is thought to be dependent on the nature of the central metal, is currently under further investigation, as is the oxygen-atom-transfer pathway for the reduction of NO_2 to NO bonded to transition metals and with the involvement of CO.

Acknowledgements

We thank the Verband der Chemischen Industrie, Stiftung Stipendien-Fonds, for a Kékulé scholarship to A. S., the SERC for funding for the diffractometer and the University of Edinburgh for support.

References

1 B. F. G. Johnson and S. Bhaduri, *J. Chem. Soc., Chem. Commun.*, 1973, 650.
2 B. F. G. Johnson, S. Bhaduri, C. J. Savoy, J. A. Segal and R. H. Walter, *J. Chem. Soc., Chem. Commun.*, 1974, 809.
3 D. R. Mantell and W. L. Gladfelter, *J. Organomet. Chem.*, 1988, **347**, 333.
4 D. M. P. Mingos and A. L. Rohl, *J. Chem. Soc., Dalton Trans.*, 1991, 3419.
5 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
6 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
7 B. F. G. Johnson, A. Sieker, A. J. Blake and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1993, 1345; *J. Organomet. Chem.*, 1994, **475**, 193.

Received 23*rd December* 1994; *Communication* 4/07823C