# The Dinitratotetracarbonylrhenate(I) Complex

By **C. Clifford Addison, Reginald Davis,** and **Norman Logan,*** Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD

Reaction of $Re(CO)_5NO_3$ with $Ph_4As^+NO_3^-$ yields the compound $Ph_4As^+[Re(CO)_4(NO_3)_2]^-$ incorporating the first reported example of a mononuclear dinitratocarbonylmetallate. I.r. spectroscopy indicates unidentate nitrate ligands in *cis*-configuration.

THE compatibility of oxidising nitrate and oxidisable carbonyl ligands within the same complex has been demonstrated by the formation of the compounds $Mn(CO)_5NO_3$ [1] and $Re(CO)_5NO_3$ [2,3] on reaction of the corresponding dimethyl decacarbonyls with dinitrogen tetroxide; $[Rh(CO)_2NO_3]_2$ has also been described,[4] but until now it has not been possible to introduce further nitrate ligands into mononuclear carbonyl species. $Mn(CO)_5NO_3$ is of low thermal stability and in the presence of an excess of liquid $N_2O_4$ all CO groups are removed, yielding $Mn(NO_3)_2$. In contrast, $Re(CO)_5NO_3$ sublimes at 100 °C without decomposition and is inert to liquid $N_2O_4$, and the existence of a dinitrato-complex seemed possible. We have found that the reaction of $Re(CO)_5NO_3$ with an equimolar amount of nitrate ion (in the form of the tetraphenylarsonium salt) under reflux in dichloromethane or chloroform yields the complex tetraphenylarsonium dinitratotetracarbonylrhenate(I), $Ph_4As^+[Re(CO)_4(NO_3)_2]^-$.

## EXPERIMENTAL

*Preparation of Tetraphenylarsonium Dinitratotetracarbonylrhenate*(I).—Nitratopentacarbonylrhenium(I), $Re(CO)_5NO_3$,[2,3] (0·542 g, 1·39 mmol) and tetraphenylarsonium nitrate (0·617 g, 1·38 mmol) were dissolved in dichloromethane (50 ml) and heated under reflux for 2 h. Removal of solvent from the dark brown solution gave a brown oil which was covered with light petroleum (b.p. 60—80°) and small quantities of chloroform or dichloromethane were added to the boiling mixture, until the oil just dissolved. After standing the resulting solution for some hours at 0 °C, a brown solid was precipitated (Found: C, 41·5; H, 2·6; N, 3·3. $C_{28}H_{20}N_2O_{10}Re$ requires C, 41·35; H, 2·45; N, 3·45%). Yields varied between 5 and 20% [based on $Re(CO)_5NO_3$] and were improved to about 60% by employing chloroform as the reaction medium and inducing

---

[1] C. C. Addison, M. Kilner, and A. Wojcicki, *J. Chem. Soc.*, 1961, 4839.

[2] C. C. Addison, R. Davis, and N. Logan, *Inorg. Chem.*, 1967, **6**, 1926.

[3] C. C. Addison, R. Davis, and N. Logan, *J. Chem. Soc.* (*A*), 1970, 3333.

[4] D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.

solidification of the oil initially obtained by covering with light petroleum (b.p. 60—80°) and allowing to stand for several hours at 0 °C.

*Spectra.*—I.r. spectra were recorded on a Perkin-Elmer 521 spectrophotometer as mulls in Nujol and Halocarbon oils between silver chloride (4000—600 cm$^{-1}$) and Polythene-protected caesium iodide (600—250 cm$^{-1}$) windows and as a chloroform solution in a silver chloride fixed path-length cell (0·1 cm).

Analyses for hydrogen, carbon, and nitrogen were obtained by standard microanalytical techniques. Electrical conductivity measurements were made by means of a Mullard conductivity bridge and a dip-type cell with bright platinum electrodes. Nitratopentacarbonylrhenium(I), $Re(CO)_5NO_3$, was prepared as described previously.[2] Tetraphenylarsonium nitrate was supplied by Dr. B. D. Faithful, Chemistry Department, University of Nottingham. Solvents were dried and purified by standard techniques.

## RESULTS AND DISCUSSION

Tetraphenylarsonium dinitratotetracarbonylrhenate(I) is not volatile and decomposes without melting at 146 °C. Its qualitative solubility characteristics parallel fairly closely those of nitratopentacarbonylrhenium(I),[2] *i.e.* $Ph_4As^+[Re(CO)_4(NO_3)_2]^-$ is soluble in most polar organic solvents, very slightly soluble in hot water and insoluble in carbon tetrachloride, hydrocarbons, and diethyl ether. A solution in nitrobenzene ($1 \times 10^{-3}$M) exhibited a molar conductivity of 26·6 $\Omega^{-1}$ cm$^2$, as expected[5] for a 1 : 1 electrolyte.

The i.r. spectrum is recorded in the Table and shows four bands in the carbonyl stretching region (chloroform solution) as predicted by group theory for a *cis*-$M(CO)_4L_2$ complex of $C_{2v}$ symmetry (for the more symmetrical *trans*-isomer, only one band is expected).[6] A shoulder at 2035 cm$^{-1}$ was also observed, perhaps as a consequence of the lowering of the overall molecular symmetry by the nitrate groups. A similar situation has been reported[3] for $Re(CO)_5NO_3$. The nitrate absorptions suggest that both groups are bonded in a unidentate manner, again as found[3] for $Re(CO)_5NO_3$.

After heating $Ph_4As^+[Re(CO)_4(NO_3)_2]^-$ to 135 °C under vacuum (0·1 mmHg) for 16 h, no change was observed in its i.r. spectrum, and we have found no experimental conditions under which isomerisation occurs.

The *cis*-configuration of the nitrate groups in $[Re(CO)_4(NO_3)_2]^-$ suggests that the lability of the CO group bonded *trans* to unidentate nitrate in $Re(CO)_5NO_3$ is low, relative to the *cis*-bonded CO groups. This is a well known effect, demonstrated by $^{14}CO$ exchange studies[7] on $Mn(CO)_5X$ compounds and attributed to the stronger back-bonding from Mn to the CO group *trans* to X, since it is necessary for the other CO groups to compete with one another for metal electrons. Dihalogenotetracarbonyl anions of manganese(I)[8] and rhenium(I)[9] are also of *cis*-configuration and the behaviour of nitrate evidently parallels that of halide ligands in such systems.

I.r. spectrum of $Ph_4As^+[Re(CO)_4(NO_3)_2]^-$

| Wavenumber/ cm$^{-1}$ [a] | | Assignment [b] |
|---|---|---|
| 3086m | | ν(CH) |
| 3062m | | |
| 3025w | | |
| 2116w | $A_1^{(2)}$ | ν(CO) |
| (2104w) | | |
| (2035sh) | | |
| 2015s | $B_1$ | |
| (2019s) | | |
| 1980m | $A_1^{(1)}$ | |
| (1977m) | | |
| 1924m | $B_2$ | |
| (1920m) | | |
| 1882s | | |
| 1597w | | $Ph_4As^+$ |
| 1579w | | |
| 1483s | | |
| 1479s | | |
| 1462s | | $A'\nu_{as}(NO_2)$ |
| 1454s | | |
| 1440sh | | $Ph_4As^+$ |
| 1436s | | |
| 1337w | | |
| 1273s,br | | $A'\nu_s(NO_2)$ |
| 1187m | | $Ph_4As^+$ |
| 1163m | | |
| 1087s | | |
| 1018m | | |
| 996s | | |
| 987m | | $A'\nu_s(NO)$ [c] |
| 976m | | |
| 842w | | $Ph_4As^+$ |
| 800w | | $A''\pi(NO_3)$ |
| 740s | | $Ph_4As^+$ |
| 688s | | |
| 666w | | |
| 642m | | $Ph_4As^+ + \delta(MCO)$ |
| 610w | | |
| 586w | | |
| 524m | | $Ph_4As^+ + \nu(MC)$ |
| 512w | | |
| 474s | | |
| 463s | | |
| 355m | | |

[a] Nujol and Halocarbon oil mulls except figures in parentheses which refer to chloroform solution. [b] Nitrate assignments refer to $C_s$ unidentate bonding; CO stretching assignments refer to a *cis*-$M(CO)_4L_2$ complex of $C_{2v}$ symmetry (ref. 6). [c] Co-ordinated oxygen.

We thank the S.R.C. for a maintenance grant (to R. D.).

[3/1820 *Received*, 3*rd September*, 1973]

---

[5] C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4375.

[6] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25; F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[7] A. Wojcicki and F. Basolo, *J. Amer. Chem. Soc.*, 1961, **83**, 525.

[8] R. J. Angelici, *Inorg. Chem.*, 1964, **3**, 1099; E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 1964, 434.

[9] E. W. Abel, I. S. Butler, M. C. Ganorkar, C. R. Jenkins, and M. H. B. Stiddard, *Inorg. Chem.*, 1966, **5**, 25.