The Thermochemistry of Chlorocarbonyl(sulfur dioxide)bis(triphenylphosphine)rhodium(I)

Sir:

Muir and Ibers[1] have recently determined the structure of the sulfur dioxide adduct of chlorocarbonylbis(triphenylphosphine)rhodium(I) the preparation of which was first reported by Vaska and Bath.[2] It shows that, in common with the isostructural iridium analog,[3] this complex has an unusually long and presumably weak metal–sulfur bond.

Using a Perkin-Elmer differential scanning calorimeter we have studied the reaction

$$\mathrm{RhCl(CO)(SO_2)(P(C_6H_5)_3)_2(c)} \longrightarrow \mathrm{RhCl(CO)(P(C_6H_5)_3)_2(c)} + \mathrm{SO_2(g)} \quad (1)$$

which occurs quantitatively over the temperature range 401–454°K. The sulfur dioxide adduct was made from chlorocarbonylbis(triphenylphosphine)rhodium (Alfa Inorganics) by the method of Muir and Ibers.[1] The quantitative nature of reaction 1 was confirmed by the agreement between the observed and calculated weight losses (both 8.5%) and by the shift of the infrared carbonyl stretching absorption from 2030 $\mathrm{cm^{-1}}$ in $\mathrm{RhCl(CO)(SO_2)(P(C_6H_5)_3)_2}$ to 1964 $\mathrm{cm^{-1}}$ in $\mathrm{RhCl(CO)(P(C_6H_5)_3)_2}$.

The enthalpy of reaction 1 at 429°K is 6.9 ± 0.2 kcal $\mathrm{mol^{-1}}$ which represents the breaking of the rhodium–sulfur bond and also the rearrangement of the remaining metal–ligand bonds. The shift of the carbonyl stretching absorption to a lower frequency during reaction 1 implies an increase in strength of the rhodium–carbon bond which, if a similar strengthening of the rhodium–phosphorus and rhodium–chloride bonds occurs, would indicate that $\Delta H(1)$ reported above is a minimum value for the rhodium–sulfur bond energy. This is well below energies of the order of 30 kcal for transition metal–sulfur bonds in, for example, crystalline thiourea complexes.[4]

It is noteworthy that $\Delta H(1)$ for the rhodium complex is slightly less than the value (8.4 ± 0.2 kcal $\mathrm{mol^{-1}}$ at 457°K) found[5] for the iridium species. The same conclusion may be drawn from the work of Moroni, Friedel, and Wender[6] (drawn to our attention by the referees), who have studied the equilibrium mixtures of gaseous $\mathrm{SO_2}$ and $\mathrm{RhCl(CO)(P(C_6H_5)_3)_2}$ or the iridium analog. The gain of $\mathrm{SO_2}$, the reverse of reaction 1, is an exothermic process and occurs less readily with the rhodium than with the iridium compound.

A greater degree of metal–sulfur back-π-bonding in the iridium complex may account for its slightly higher bond energy, but π bonding is considered[1] to be only of minor importance in these complexes.

Vaska[7] has given thermodynamic data for the formation of the $\mathrm{O_2}$ and $\mathrm{SO_2}$ adducts of $\mathrm{IrCl(CO)(P(C_6H_5)_3)_2}$, but these refer to chlorobenzene solution, so that it is difficult to make direct comparison with our results[5] for the crystalline complexes.

We can find no report in the literature on the preparation of a molecular oxygen complex of chlorocarbonylbis(triphenylphosphine)rhodium similar to that formed by the corresponding iridium compound,[8] although we have evidence that it is formed to some extent on bubbling oxygen through a solution of $\mathrm{RhCl(CO)(P(C_6H_5)_3)_2}$ in dry benzene, first under reflux for 0.5 hr and then at room temperature for a further 16 hr. Evaporation of the solvent yields a buff solid having a C–H analysis intermediate between the values expected for the oxygen adduct and the parent compound. The possibility that this solid may be a mixture of the two complexes is further strengthened by the appearance of a strong infrared absorption at 1983 $\mathrm{cm^{-1}}$ in addition to the carbonyl absorption at 1964 $\mathrm{cm^{-1}}$ associated with the parent compound. When examined in the scanning calorimeter, the mixture resembles the oxygen adduct of the iridium parent[5] compound in that it decomposes exothermically at 432°K whereas the pure parent rhodium compound does not show any thermal effects until the onset of melting and exothermic decomposition at 468°K. The lower reactivity of $\mathrm{RhCl(CO)(P(C_6H_5)_3)_2}$ toward oxygen may be an indication that metal–ligand back-π-bonding, as discussed by McGinnety, Doedens, and Ibers[9] and as suggested by the above thermochemical data on rhodium– and iridium–sulfur bond strengths, is likely to be a less significant bond strengthening factor in a rhodium–oxygen complex than in the iridium analog.

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(8) L. Vaska, *Science*, **140**, 809 (1963).
(9) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).
(10) Address correspondence to this author at the University of Keele.

Department of Chemistry C. T. Mortimer*[10]
The University of Keele
Keele, Staffordshire ST5 5BG,
England

Department of Chemical Engineering S. J. Ashcroft
The University of Exeter
Exeter, England

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Additions and Corrections

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Charles B. Roberts and Darell D. Toner: Dihydrotrimethylsiloxyaluminum.

Page 2361. The first word in the bottom line of the text, first column, should read hexamethyldisilazane instead of trimethylsilazane.

Page 2362. In the next to the last line of the Acknowledgment, trimethyltriazane should read hexamethyldisilazane.

Mazhar-Ul-Haque, Charles N. Caughlan, and Ken Emerson: The Crystal and Molecular Structure of Tris(ethylenediamine)nickel(II) Sulfate, $\mathrm{Ni(NH_2CH_2CH_2NH_2)_3SO_4}$.

Page 2422. The *z* coordinate of atom O(4) in Table I is given as 0.358 (3); it should read 0.368 (3). In Table II, part IV, the labels for the two groups of H bonds have been interchanged; group A are equatorial H bonds and group B are axial H bonds.

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