E.S.R. Study of the Cation Radical of $Rh_2(O_2CEt)_4(PPh_3)_2$; a σ Electron Radical

By TAKASHI KAWAMURA,* KADZUHIKO FUKAMACHI, and SHIGERU HAYASHIDA
(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto* 606, *Japan*)

Summary Electrochemical or radiochemical oxidation of $Rh_2(O_2CEt)_4(PPh_3)_2$ gives its cation radical, the e.s.r. spectra of which reveal that the odd electron orbital has σ symmetry with respect to the P–Rh–Rh–P axis and that the odd electron is distributed over the phosphorus and rhodium atoms.

THERE has been considerable controversy regarding the multiplicity of the short metal-metal bond in dirhodium tetracarboxylates.[1–3] A triple bond[1] with a configuration of $\sigma^2\pi^4\delta^2\delta^{*2}\sigma_n'^2\sigma_n^2$ and a single bond[2,3] with a $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ configuration have been proposed. Recent studies[4] on the stability of $[Rh_2(O_2CMe)_4(H_2O)_2]^{+\bullet}$ have suggested that e.s.r. spectroscopy can contribute[5] to an understanding of the electronic structure of the Rh–Rh bond.

Cyclic voltammetry of $Rh_2(O_2CEt)_4(PPh_3)_2$[6] in CH_2Cl_2† showed a quasi-reversible one-electron (coulometry, $n = 1{\cdot}0 \pm 0{\cdot}1$) oxidation wave at $E_{3/4p}$ 0·60 V *vs.* standard calomel electrode (s.c.e.); $E_{pa} - E_{pc} = 72 \pm 5$ mV and $i_{pa}/i_{pc} = 1{\cdot}0 \pm 0{\cdot}1$.

Electrochemical oxidation of the dirhodium complex in CH_2Cl_2 solution containing $Bu^n{}_4NClO_4$ on an Au anode at 0·75 V *vs.* s.c.e. at −20 °C gave a reddish-purple solution (λ_{max} 525 nm) whose e.s.r. spectrum showed a broad triplet of 16·8 mT with a g factor of 2·109. When the solution was frozen and subjected to e.s.r. spectroscopy at −170 °C, the spectrum of an axially symmetric species was observed (Figure); the ⊥ component was a triplet (15·1 mT) with $g_\perp = 2{\cdot}157$ and the ∥ component was a triple triplet (21·7 and 1·47 mT) with $g_\parallel = 1{\cdot}994$.‡ The same solid phase spectrum was observed at −196 °C from a γ-irradiated Freon mixture (1:1 v/v CF_2BrCF_2Br and $CFCl_3$) glass containing the dirhodium complex. The solid Freon mixture is known to be an appropriate matrix for trapping cationic species formed from a solute upon radiolysis.[7]

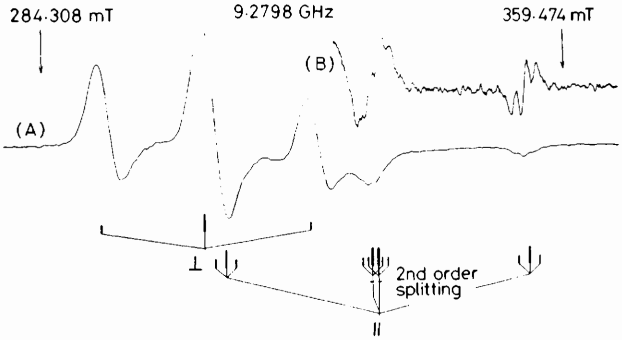

FIGURE. First derivative (A) and second derivative (B) e.s.r. spectra of $[Rh_2(O_2CEt)_4(PPh_3)_2]^{+\bullet}$ electrochemically generated in CH_2Cl_2 and observed at −170 °C.

The paramagnetic species has two pairs of equivalent nuclei both with $I = 1/2$ ($I = 1/2$ for ^{31}P and ^{103}Rh) and is thus attributed to $[Rh_2(O_2CEt)_4(PPh_3)_2]^{+\bullet}$. A comparison of fluid and solid phase spectra shows that the anisotropic couplings of 15·1 (⊥ component) and 21·7 mT (∥ component) are due to a pair of equivalent nuclei of $I = 1/2$ and that they have the same sign which is tentatively assumed to be

---

† Dirhodium complex 0·5 mmol l^{-1}; $Bu^n{}_4NClO_4$ 0·15 mol l^{-1}; Pt wire working electrode; potential sweep 60 mV s^{-1}. The authors are indebted to Professor K. Okamoto and Dr. K. Komatsu for cyclic voltammetry instruments.

‡ E.s.r. spectra were analysed to the second order with respect to the hyperfine interactions.

positive. The isotropic and anisotropic parts of the coupling are $a = 17{\cdot}3$ and $2b = 4{\cdot}4$ mT, respectively. This coupling anisotropy is greater than that of ^{103}Rh with a 4*d* spin density of 1/2.[8] The largest triplet splitting is, therefore, assigned to the pair of ^{31}P nuclei. Odd electron densities on the 3*s* and 3*p* orbitals on each phosphorus atom are estimated as $\rho(\mathrm{P}, 3s) = 17{\cdot}3/368 = 0{\cdot}047$ and $\rho(\mathrm{P}, 3p) = 4{\cdot}4/20{\cdot}2 = 0{\cdot}22$.[8] The large odd electron density on the phosphorus atoms (total 53%) and the inequality of $a_{\parallel}(\mathrm{P}) > a_{\perp}(\mathrm{P})$ are consistent only with the odd electron orbital consisting of phosphine lone pair orbitals; the odd electron orbital has σ symmetry with respect to the P–Rh–Rh–P axis. The usual approximate treatment[8] of the ratio of $\rho(\mathrm{P}, 3p)/\rho(\mathrm{P}, 3s)$ gave a C–P–C bond angle of 112°, which is between that of triphenylphosphine (103°)[9] and those of cation radicals of phosphines (*ca.* 115°),[10] as expected.

The σ symmetry (a_{1g} or a_{2u} in an approximate point group of D_{4h}) of the odd electron orbital is consistent also with the observed $g_{\parallel}$ which is not very different from the free spin *g* factor (2·002). The positive shift of $g_{\perp}$ from 2·002, far larger than the corresponding shifts observed for $(\mathrm{PR_3})^{+\cdot}$ and $[(\mathrm{PR_3})_2]^{+\cdot}$[10] should have been induced by excitations of electrons in π or π^* (e_u or e_g in D_{4h}) orbitals with appreciable metal character to the metal part of the odd electron orbital through L–S couplings. The odd electron orbital is thus concluded to consist of phosphine lone pair orbitals (*ca.* 50%) as well as of metal orbitals with σ symmetry with respect to the molecular axis.

At a glance this result supports the triple bond model[1] with the highest occupied orbital of σ_n or σ_n'. However, this result is also consistent with the single bond model[2] if the Rh–Rh σ bonding orbital [corresponding to the $8a_g$ orbital of $\mathrm{Rh_2(O_2CH)_4(H_2O)_2}$ in ref. 2] is the highest occupied orbital; SCF-Xα-SW calculations suggest that the Rh–Rh σ bonding orbital of $\mathrm{Rh_2(O_2CH)_4L_2}$ attains Rh–L antibonding character and shifts upward in energy when L is a strong σ electron donor.[2,3§]

(*Received, 19th June* 1979; *Com.* 651.)

---

§ The energy difference between the $8a_g$ (σ) orbital and the highest occupied orbital, $7b_{1u}$ (δ^*), calculated for $\mathrm{Rh_2(O_2CH)_4(H_2O)_2}$ by the SCF-Xα-SW method was 1·4 eV (see reference 2).

[1] K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, 1971, **93**, 1914.

[2] J. G. Norman, Jr. and H. J. Kolari, *J. Amer. Chem. Soc.*, 1978, **100**, 791.

[3] G. G. Christoph and Y.-B. Koh, *J. Amer. Chem. Soc.*, 1979, **101**, 1422.

[4] C. R. Wilson and H. Taube, *Inorg. Chem.*, 1975, **14**, 2276; R. D. Cannon, D. B. Powell, K. Sarawek, and J. S. Stillman, *J.C.S. Chem. Comm.*, 1976, 31; J. J. Ziółkowski, M. Moszner, and T. Glowiak, *ibid.*, 1977, 760.

[5] *Cf.* S. W. Bratt and M. C. R. Symons, *J.C.S. Dalton*, 1977, 1314 and references cited therein.

[6] T. A. Stephenson, S. M. Morehouse, A. P. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[7] A. Grimison and G. A. Simpson, *J. Phys. Chem.*, 1968, **72**, 1776; T. Shida, Y. Nosaka, and T. Kato, *ibid.*, 1978, **82**, 695.

[8] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[9] J. J. Daly, *J. Chem. Soc.*, 1964, 3799.

[10] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1971, 2290; *J.C.S. Faraday II*, 1972, **68**, 1589.