Electron Spin Resonance and Electrochemical Studies of Monocyclopentadienyl-titanium(III) and -zirconium(III) Derivatives $[M(\eta^5-C_5H_5)R_2]$ involving Chelated Phosphinomethyl (R = CH_2PPh_2) and Phosphinoacetate (R = $O_2CCH_2PPh_2$) Ligands

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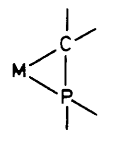
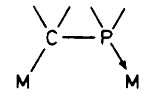
E.s.r. and electrochemical techniques demonstrate that the $^-CH_2PPh_2$ group bonded to Ti^{III} and Zr^{III} gives a three-membered ring and a five-membered ring is obtained when $^-O_2CCH_2PPh_2$ is bonded to Zr^{III}; opening of the ring is achieved by co-ordination of the phosphorus atom to another metal (Mo) yielding a heterobimetallic complex.

Cyclometallation of phosphines is well documented in the late transition metal chemistry, giving structure (I) (M = Rh, Ir, Pd, Pt, *etc.*).[1] In the field of early transition metals, Schore and Hope[2] prepared the phosphinomethyl derivative $[ZrCl(cp)_2(CH_2PPh_2)]$ (1) (cp = η-cyclopentadienyl) which gave a species formulated as $[ZrCl_x(cp)_2(CH_2PPh_2)]^{x-}$ (2) (x = 0 or 1) by Na/Hg reduction. The e.s.r. spectrum of (2) exhibits a superhyperfine coupling constant to the phosphorus [$a(^{31}P)$ = 19.5 G] which demonstrates structure (I) in this zirconium(III) derivative. No coupling to the protons of the methylene group can be detected on the spectrum.

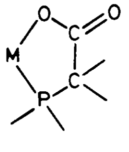
We now report the e.s.r. study of species obtained by chemical or electrochemical reduction of $[Ti(cp)_2R_2]$ and $[Zr(cp)_2R_2]$ derivatives where R is either the diphenylphosphinomethyl group, $^-CH_2PPh_2$, previously used by Schore and Hope[2] or the diphenylphosphinoacetate group, $^-O_2CCH_2PPh_2$.



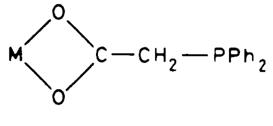
(I)



(II)



(III)



(IV)

Table. E.s.r. data in thf solution at room temperature

Starting material	g	$a(^{31}P)$ [a]	$a(^1H)$ [a]	$A(M)$ [a,b]
$[Ti(cp)_2(CH_2PPh_2)_2]$	1.986	9.8	2.5	10.3
$[Zr(cp)_2(CH_2PPh_2)_2]$	1.987	16.1	2.8	22.5
$[Zr(cp)_2(O_2CCH_2PPh_2)_2]$	1.987	11.8	—	22.9
$[Ti(cp)_2(CH_2Ph)_2]$ [c]	1.998	—	2.12	8.37
$[Zr(cp)_2(CH_2Ph)_2]$ [c]	1.986	—	2.45	17.5

[a] All values in Gauss (G = 10^{-4} T). [b] Hyperfine coupling to ^{47}Ti ($I = \frac{5}{2}$, 7.75% natural abundance), ^{49}Ti ($I = \frac{7}{2}$, 5.51%), and ^{91}Zr ($I = \frac{5}{2}$, 11.23%). [c] Ref. 3.

Results and Discussion

Two examples of room-temperature e.s.r. spectra of the reduced species obtained by reaction of $[M(cp)_2R_2]$ with sodium dihydronaphthylide in tetrahydrofuran (thf) solution are shown in the Figure. Chemical and electrochemical reduction of $[Ti(cp)_2(CH_2PPh_2)_2]$ gave exactly the same spectrum, quite similar to Figure (*a*). E.s.r. parameters are reported in the Table and compared with literature data.[3] In every case a central 1 : 2 : 1 triplet is observed, due to the coupling to two equivalent phosphorus atoms.

When R = CH_2PPh_2 and M = Ti or Zr, each line of the triplet is split by coupling to four equivalent protons. The coupling constant is consistent with co-ordination of the phosphorus atoms to the metal,[2,4] with the arrangement (I). This ruled out the formation of $[M(cp)_2R_2]^-$ because of the excess of electrons on the metal and supports the formation of a stable monocyclopentadienyl species $[M(cp)R_2]$ from the unstable $[M(cp)_2R_2]^-$ formed in the first step of the reduction, as was previously discussed by El Murr and co-workers[5] and Lappert *et al.*[3] The anodic peak attributable to the oxidation of the dissociated cyclopentadienyl anion can be seen at −0.230 V in the cyclic voltammogram performed on the reduced solution after electrolysis of $[Ti(cp)_2(CH_2PPh_2)_2]$.

Moreover, opening of these three-membered metallated rings (I) appeared to be performed in the presence of another metal M′ (*e.g.* Mo) with more affinity for phosphorus than M (Ti or Zr) and is evidenced by the disappearance of the coupling of the electron to phosphorus. For instance, addition of $[Mo(CO)_6]$ to the reduced solution obtained from $[Ti(cp)_2(CH_2PPh_2)_2]$ results in the evolution of the e.s.r. spectrum from Figure (*a*) to a singlet (g = 1.981) only accompanied by the expected satellites due to ^{47}Ti and ^{49}Ti, which is explained by the bridged bimetallic arrangement (II).

When R = $O_2CCH_2PPh_2$ and M = Zr, the 1 : 2 : 1 triplet due to coupling to the two phosphorus atoms still remains but no coupling to protons can be seen [Figure (*b*)]. This rules out $[M(cp)_2R_2]^-$ formation and is compatible with $[M(cp)R_2]^-$ formation, giving five-membered cyclometallation of the ligand [arrangement (III)] as was previously reported by Manzer[6] in the case of alike N-donor ligands. It is noteworthy that, on account of oxophilicity and 'class a' behaviour[7] of zirconium, chelation *via* the phosphorus atom in preference to the oxygen atom [arrangement (IV)] was unexpected.

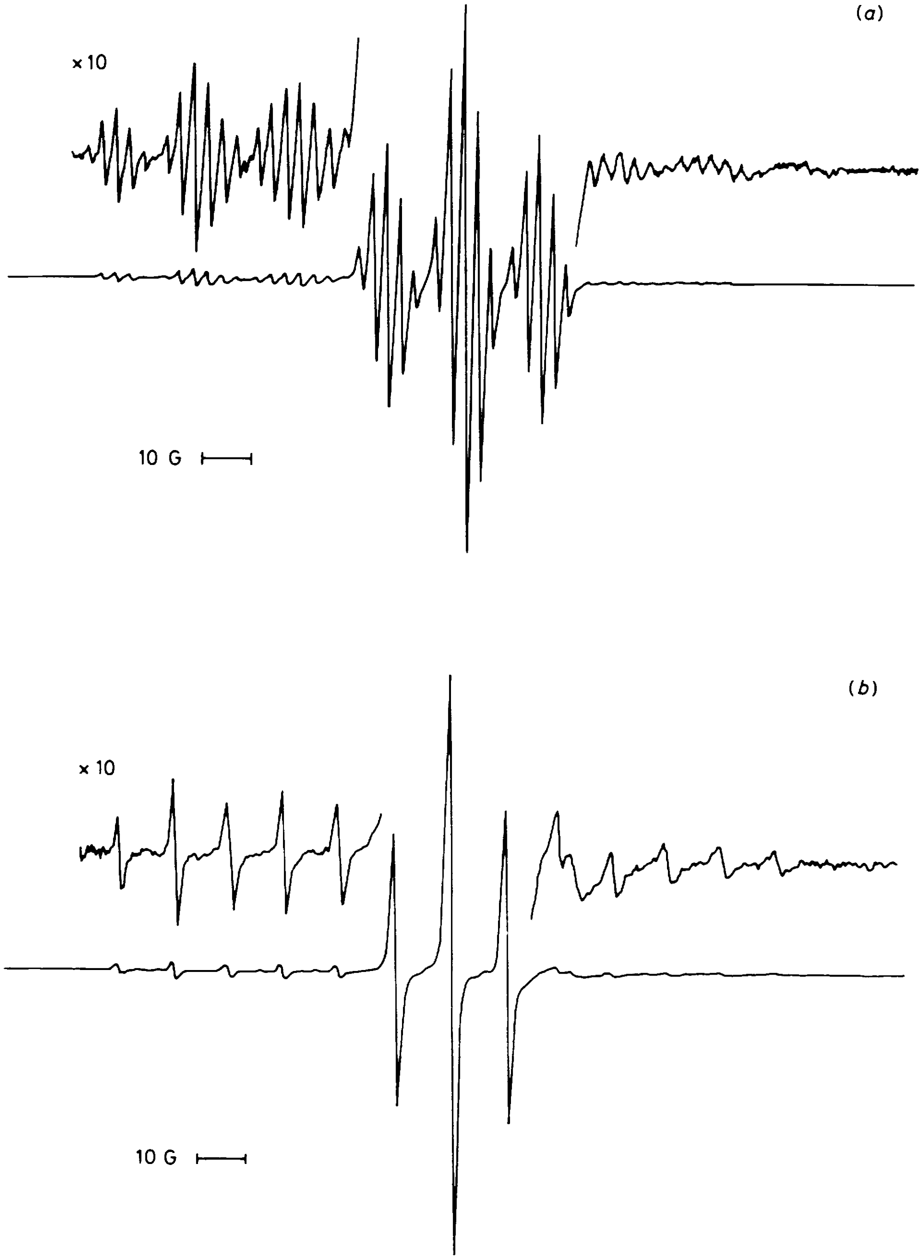


Figure. *X*-Band e.s.r. spectra of reduced thf solutions of $[M(cp)_2R_2]$: (*a*) $[Zr(cp)_2(CH_2PPh_2)_2]$; (*b*) $[Zr(cp)_2(O_2CCH_2PPh_2)_2]$

Experimental

All reactions were carried out under argon using carefully distilled and degassed solvent, in conventional Schlenk apparatus.

Electrochemical measurements as well as controlled-potential electrolysis were performed in thf with $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) as supporting electrolyte at a Pt disc working electrode. The auxiliary electrode was a Pt wire and the potentials were referred to Ag/Ag^+ [Ag wire in aqueous solution of KCl (0.1 mol dm^{-3})–saturated AgCl].

Cyclic voltammograms were recorded before and after electrolysis of a 10^{-3} mol dm^{-3} solution of $[Ti(cp)_2(CH_2PPh_2)_2]$ at a scan rate of 0.3 V s^{-1}.

Chemical Reduction.—All the reduced compounds were obtained by the same method. For example, to 70 mg (1.2 × 10^{-4} mol) of $[Ti(cp)_2(CH_2PPh_2)_2]$ in thf (3 cm^3), one equivalent of a green thf solution of sodium dihydronaphthylide was added dropwise *via* a syringe under argon. The e.s.r. spectrum was recorded after *ca.* 5 min on the resulting brown-red and very air-sensitive solution.

$[Zr(cp)_2(CH_2PPh_2)_2]$ was prepared according to the method of Schore and Hope.[2] $[Ti(cp)_2(CH_2PPh_2)_2]$ was obtained by a similar way by reacting $Li[CH_2PPh_2]$ with $[TiCl_2(cp)_2]$ in thf (Found: C, 74.2; H, 5.9; P, 10.8; Ti, 8.3. $C_{36}H_{34}P_2Ti$ requires C, 75.0; H, 5.9; P, 10.5; Ti, 8.4%). ^1H N.m.r. (C_6D_6): δ 5.9 (10 H, s, C_5H_5), 1.65 (4 H, d, $^2J_{PH}$ = 3.5 Hz, CH_2).

$[Zr(cp)_2(O_2CCH_2PPh_2)_2]$ was prepared by reaction of carbon dioxide (10^5 Pa) with $[Zr(cp)_2(CH_2PPh_2)_2]$ at room temperature. Two mol of CO_2 were absorbed and a white solid was obtained (Found: C, 63.8; H, 4.8. $C_{38}H_{34}O_4P_2Zr$ requires C, 64.5; H, 4.8%). ^1H N.m.r. (C_6D_6): δ 6.0 (10 H, s,

C_5H_5), 3.2 (4 H, unresolved). I.r. (thf solution): $\nu(CO_2)$ 1 550 and 1 370 cm^{-1}.

Acknowledgements

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