DALTON

Electron spin resonance study of the frozen-solution equilibrium $[Co\{S_2C_2(CF_3)_2\}_2L] + L \rightleftharpoons [Co\{S_2C_2(CF_3)_2\}_2L_2]$ $[L = P(OR)_3$ or $PPh(OMe)_2$; $R =$ alkyl] †

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The ESR spectra have been recorded for a series of cobalt dithiolene complexes $[Co(S_2C_2R_2)_2L]$ [$R = CF_3$; $L = P(OMe)_3$, $P(OEt)_3$, $P(OBu^n)_3$ or $PPh(OMe)_2$]. In toluene, tetrahydrofuran or CH_2Cl_2–1,2-$C_2H_4Cl_2$ solutions containing a small excess of L, reversible spectral changes are observed between 165 and 130 K which correspond to the addition of a second ligand to form a six-co-ordinate complex. For $L = P(OMe)_3$ in toluene, equilibrium constants were estimated from the spectra which lead to $\Delta H^\circ = -10$ kJ mol^{-1}, $\Delta S^\circ = -68$ J K^{-1} mol^{-1} for the five-/six-co-ordinate equilibrium. Ligand addition is not observed when CF_3 is replaced by Ph, 4-MeC_6H_4 or 4-$MeOC_6H_4$ or $L = PPh_3$, PEt_3, $P(OPr^i)_3$, $P(OCH_2CF_3)_3$ or $P(OPh)_3$. Complexes with $L = (Ph_2P)_2CH_2$, $(Ph_2PCH_2)_2$ or $[(MeO)_2PCH_2]_2$ are five-co-ordinate with no evidence for chelation. Thus both steric and electronic effects are critical to the ability of the five-co-ordinate complex to add a sixth ligand. Unlike the five-co-ordinate complexes which are significantly distorted from ideal C_{2v} symmetry, the six-co-ordinate complexes are highly symmetrical with greater delocalization of the unpaired electron onto the phosphite ligands.

There was considerable interest in the 1960s and 1970s in the reversible addition of Lewis bases to square-planar, *e.g.* nickel(II)[2] and copper(II),[3] and square-pyramidal, *e.g.* oxovanadium(IV)[4] and oxorhenium(VI),[5] and chloromanganese(III)[6] complexes. Many such adducts were characterized spectroscopically, equilibrium constants for adduct formation were measured, and in several cases ESR linewidth studies were carried out to determine the rates of adduct formation.[7] It was usually assumed that a Lewis base adds to a square-pyramidal complex such as $[VO(acac)_2]$ (acac = acetylacetonate) at a position *trans* to the oxo ligand, but Kirste and van Willigen[8] used ENDOR (electron nuclear double resonance) spectra to show that pyridine adds *cis* and that other bases give a mixture of the *cis* and *trans* isomers.

The same period also saw a lot of work on square-pyramidal dithiolene complexes of iron and cobalt,[9] and a series of papers by Yablokov, Ryzhmanova and co-workers[10] reported an ESR study of $[Co(S_2C_2Ph_2)_2L]$ in the presence of an excess of L [$= P(OEt)_3$, $PEt(OEt)_2$, $PEt_2(OEt)$ as well as several other phosphites, phosphonites and phosphinites]. They found that a reaction occurs to form sequentially two ESR-active products, identified as the *trans* and *cis* six-co-ordinate complexes. The Russian work differs from that described above in that the addition reactions were apparently slow and irreversible.

Here we report ESR evidence for the reversible formation of *trans*-$[Co\{S_2C_2(CF_3)_2\}_2L_2]$ [$L = P(OMe)_3$, $P(OEt)_3$, $P(OBu^n)_3$ or $PPh(OMe)_2$] which exhibit spectra very different from those observed by the Russian workers. The thermodynamic parameters for adduct formation are analogous to those observed in earlier work for complexes of Cu^{2+} and VO^{2+}, but the adducts are formed in detectable amounts only at temperatures well below the freezing point of the solvents used.

Experimental

Chemicals

Chlorinated solvents were distilled from calcium hydride under nitrogen; hydrocarbons were dried over sodium; tetrahydrofuran (thf) and diethyl ether were distilled from a sodium–benzophenone solution. The phosphines and phosphites were supplied by Aldrich and used as received; liquids were either from freshly opened bottles or from bottles stored under nitrogen. The bifunctional phosphonite $[(MeO)_2PCH_2]_2$ was prepared by the method of King and Rhee.[11] The complexes $[Co(S_2C_2R_2)_2L]$ were prepared from $[\{Co(S_2C_2R_2)_2\}_2]$ as described earlier[1,12] and characterized by mass spectra which showed a parent-ion peak as well as a major fragment corresponding to $[Co(S_2C_2R_2)_2]_2$.

The ESR samples were prepared by weighing a sample of the complex into a known amount of degassed solvent under argon or nitrogen and adding an appropriate amount of the phosphine or phosphite with a microsyringe. The sample was transferred to an ESR tube under an inert atmosphere using a gas-tight syringe; the tube was capped and sealed with Parafilm.

Spectroscopy

The ESR spectra were obtained with a Bruker ER-220D X-band spectrometer, equipped with a Bruker variable-temperature accessory, a Bruker gaussmeter, a Systron-Donner microwave frequency counter, and an ASPECT-2000 computer. Mass spectra were recorded with a Kratos MS80RFA spectrometer in positive-ion mode with fast atom bombardment using *m*-nitrobenzyl alcohol as a matrix.

Results

ESR spectra

The ESR spectra of $[Co(S_2C_2R_2)_2L]$ {$R = CF_3$, Ph, 4-MeC_6H_4 or 4-$MeOC_6H_4$; $L = P(OMe)_3$, $P(OEt)_3$, $P(OBu^n)_3$, $P(OPr^i)_3$, $P(OCH_2CF_3)_3$, $PPh(OMe)_2$, $(Ph_2P)_2CH_2$ (dppm), $(Ph_2PCH_2)_2$ (dppe) or $[(MeO)_2PCH_2]_2$}, in toluene, thf or CH_2Cl_2–1,2-$C_2H_4Cl_2$ solutions are very similar to those of the phosphine derivatives reported earlier.[1] Isotropic spectra consist of an octet (^{59}Co, $I = \frac{7}{2}$) of doublets (^{31}P, $I = \frac{1}{2}$); the doublet splitting was unresolved in spectra of the phosphine derivatives. Spectra of the frozen solutions show eight major

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† Dithiolenes revisited. Part 2.[1]

Non-SI unit employed: G = 10^{-4} T.

Table 1 The ESR parameters[a]

(*a*) Five-co-ordinate complexes $[Co(S_2C_2R_2)_2L]$

L	R	$\langle g \rangle$	$\langle A^{Co} \rangle$	$\langle A^{P} \rangle$	g_x	g_y	A_y^{Co}	$\alpha/°$
PPh_3[b,c]	CF_3	2.019	27.3	—	1.992	2.031	69.0	16 ± 1
$P(OPh)_3$[b,c]	CF_3	2.015	24.8	7.9	1.996[d]	2.040	59.1	11 ± 5
$P(OMe)_3$	CF_3	2.019	25.1	11.5	2.005	2.030	61.5	18 ± 1
$P(OMe)_3$[c]	CF_3	2.020	25.1	11.8	2.003	2.031	61.8	14 ± 4
$P(OMe)_3$[e]	CF_3	2.020	25.2	12.0	2.004	2.032	62.0	17 ± 7
$P(OEt)_3$	CF_3	2.018	25.2	11.5	2.004	2.035	60.4	18 ± 1
$P(OBu^n)_3$	CF_3	2.020	25.2	11.6	2.003	2.033	62.2	18 ± 1
$PPh(OMe)_2$	CF_3	2.022	25.3	8.6	2.013[d]	2.034	63.4	17 ± 5
$P(OPr^i)_3$	CF_3	2.021	25.4	12.0	1.998	2.032	62.7	5 ± 2
$P(OCH_2CF_3)_3$	CF_3	2.015	24.8	9.8	1.987[d]	2.020	59.7	3 ± 5
$[(MeO)_2PCH_2]_2$	CF_3	2.020	25.6	8.1	2.009	2.034	62.2	19 ± 2
$P(OMe)_3$	Ph	2.015	22.1	9.6	2.001	2.017	52.6	15 ± 2
dppm	$4-MeOC_6H_4$	2.012	24.0	—	1.987[d]	2.023	61.8	30 ± 4
dppe	$4-MeOC_6H_4$	2.012	24.3	—	2.018	2.022	60.0	22 ± 1
$P(OMe)_3$[c]	$4-MeOC_6H_4$	2.013	21.6	8.7	2.010	2.012	52.4	6 ± 3
$P(OEt)_3$	$4-MeOC_6H_4$	2.019	21.7	9.1	2.002	2.028	52.3	8 ± 6

(*b*) Six-co-ordinate complexes $[Co\{S_2C_2(CF_3)_2\}_2L_2]$

L	g_x	g_y	g_z	A_y^{Co}	A_y^{P}
$P(OMe)_3$	2.015	2.028	2.038	46.5	47.5
$P(OMe)_3$[e]	2.013	2.028	2.041	46.3	43.8
$P(OBu^n)_3$	2.016[d]	2.029	2.044[d]	46.5	44.8
$PPh(OMe)_2$	2.017[d]	2.029	2.045[d]	45.9	40.5

[a] Hyperfine couplings in units of 10^{-4} cm^{-1}, in toluene unless otherwise noted. [b] Data from ref. 1. [c] In CH_2Cl_2–1,2-$C_2H_4Cl_2$. [d] ±0.003. [e] In thf.

features; although the ^{31}P hyperfine structure was usually unresolved, the line shapes in spectra of the phosphite derivatives suggest couplings comparable to those observed in the isotropic spectra. As in spectra of the phosphine derivatives, the six outer features are unequally spaced due to the non-coincidence of the *x* and *y* axes of the ^{59}Co hyperfine matrix and the *g* matrix. These features can be fitted to obtain one of the components of the hyperfine matrix, two of the components of the *g* matrix, and the Euler angle α which relates the hyperfine and *g*-matrix principal axes. Detailed comparison of experimental and simulated spectra allows determination of the third *g*-matrix component, but the remaining hyperfine components can only be estimated from the isotropic value. Spin-Hamiltonian parameters are given in Table 1 and a computer-simulated spectrum for L = $P(OMe)_3$ is shown in Fig. 2(*a*).

The ESR spectra of $[Co\{S_2C_2(CF_3)_2\}_2L]$ [L = $P(OMe)_3$, $P(OEt)_3$, $P(OBu^n)_3$ or $PPh(OMe)_2$], in toluene, thf or CH_2Cl_2–1,2-$C_2H_4Cl_2$ containing a small excess of L ([complex] ≈ 0.01, [L] ≈ 0.02–0.04 mol dm^{-3}) are very similar to spectra of the pure complexes at temperatures above 160 K, but as the temperature is decreased some features disappear and others grow in until, at *ca.* 130 K and below, a qualitatively different spectrum is obtained. The temperature dependence is entirely reversible, and, except for variations associated with the quality of the glass, is easily reproducible. This process is shown for L = $P(OMe)_3$ in toluene in Fig. 1.

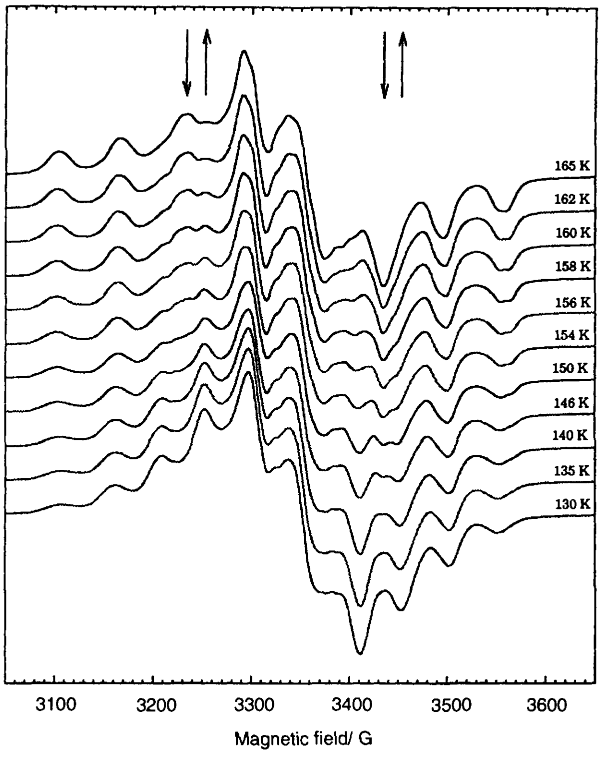

Fig. 1 The ESR spectra of $[Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}]$ in toluene solution in the presence of a small excess of $P(OMe)_3$; down- and up-pointing arrows refer to features 3 and 6 of the five-co-ordinate species and to features 4 and 8 of the six-co-ordinate species, respectively

Spectra of $[Co\{S_2C_2(CF_3)_2\}_2L]$ [L = $P(OPh)_3$, $P(OPr^i)_3$, $P(OCH_2CF_3)_3$, PPh_3 or PEt_3] were not affected by the presence of an excess of L and were essentially independent of temperature below 170 K. Those of $[Co(S_2C_2R_2)_2\{P(OMe)_3\}]$ (R = Ph, 4-MeC_6H_4 or 4-$MeOC_6H_4$) were similarly independent of the presence of an excess of $P(OMe)_3$ and temperature.

Ligand displacement occurs readily in solution. Thus, in toluene solution containing an excess of $P(OMe)_3$, $[Co\{S_2C_2(CF_3)_2\}_2\{P(OCH_2CF_3)_3\}]$ gave an isotropic spectrum identical to that of $[Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}]$ and frozen-solution spectra essentially identical to those shown in Fig. 1.

The low-temperature spectra, which we assign to $[Co\{S_2C_2(CF_3)_2\}_2L_2]$, show 10 major features with the extra features due to coupling to two equivalent ^{31}P nuclei. Although the outer features are not exactly evenly spaced, the variation is not consistent with non-coincident *g* and ^{59}Co hyperfine principal axes, but can be understood if the major ^{59}Co hyperfine component is slightly different from the corresponding ^{31}P hyperfine coupling. The variation in amplitude seen in the outer features is easily understood by this assignment: the low-field feature corresponds to $m_{Co} = \frac{7}{2}$, $m_P = 1$, the second feature to ($\frac{7}{2}$, 0) and ($\frac{5}{2}$, 1), the third to ($\frac{7}{2}$, −1), ($\frac{5}{2}$, 0) and ($\frac{3}{2}$, 1), and the fourth to $(\frac{5}{2}, -1)$, $(\frac{3}{2}, 0)$, $(\frac{1}{2}, 1)$, as well as the $m_P = 1$ components of g_z. Detailed fitting of computer simulations to these low-temperature spectra resulted in the parameters given in Table 1(*b*). A simulated spectrum for L = $P(OMe)_3$ is shown in Fig. 2(*b*).

Thermodynamic parameters for ligand association

Once the high- and low-temperature limiting spectra were understood, spectra at intermediate temperatures are easily interpreted, at least qualitatively. Thus, for example, features 4 and 8 of the six-co-ordinate species (amplitudes $A_{6,4}$ and $A_{6,8}$) grow in and replace features 3 and 6, respectively, of the five-co-ordinate species. The relative amplitudes, $A_{6,4}/A_{5,3}$ and $A_{6,8}/A_{5,6}$, then were measured for intermediate-temperature spectra, the first ratio in the range 148–165 K and the second in the range 146–154 K. These ratios were then calibrated by the relative amplitudes at the fields of these features using the computer simulations of Fig. 2. In this way values of the apparent equilibrium constant, *K*, were found [equation (1)]. A

$$K = [\mathrm{Co(dithiolene)_2L_2}]/[\mathrm{Co(dithiolene)_2L}] \qquad (1)$$

van't Hoff plot of ln *K vs.* 1/*T* (Fig. 3) is acceptably linear with points from both sets of amplitude ratios falling on the same line. The slope and intercept of the plot give $\Delta H^\circ = -10$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^\circ = -68$ J $\mathrm{K^{-1}\,mol^{-1}}$. Although the fit appears to be very good indeed, the calibration is quite sensitive to the linewidths used in the computer-simulated spectra. We assumed constant widths, chosen to fit best the spectra of the pure five-co-ordinate complex at 120 K and the low-temperature-limiting spectrum of the six-co-ordinate complex at 110 K. Although there is no evidence of temperature-dependent linewidths, even small variations would have a significant effect on the apparent equilibrium constants; thus the thermodynamic parameters are probably good to no better than ±50%.

Comparing the spectra shown in Fig. 1 with those of the five-co-ordinate complex in the absence of an excess of the ligand, there is no evidence of line broadening due to kinetic effects, *i.e.* the rate is in the slow-exchange limit of the modified Bloch equations, $\tau^{-1} \ll T_2^{-1}$.[13] With a component linewidth in the order of 5 G ($T_2^{-1} \approx 10^8$ $\mathrm{s^{-1}}$), the species lifetimes are apparently significantly greater than 10 ns in the 130–150 K temperature range, suggesting an activation free energy greater than 12 kJ $\mathrm{mol^{-1}}$.

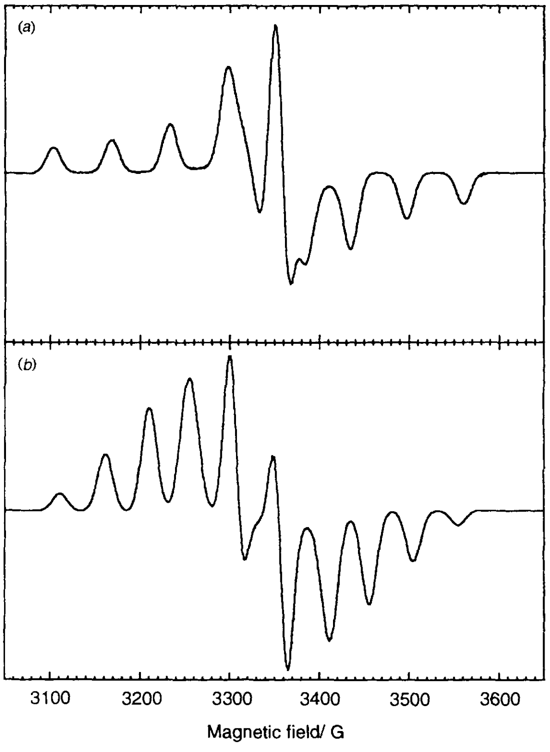

Fig. 2 Computer-simulated ESR spectra of (*a*) $[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}}]$ and (*b*) $[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}_2}]$, using the parameters of Table 1

Although the other ligand association equilibria were not studied in detail, the qualitative behaviour was similar for L = $P(OEt)_3$, $P(OBu^n)_3$ and $PPh(OMe)_2$ in toluene, thf and CH_2Cl_2–1,2-$C_2H_4Cl_2$ solutions, and the thermodynamic parameters are apparently very similar.

Electronic structure

The metal contribution to the singly occupied molecular orbital (SOMO) in the five-co-ordinate complex is primarily $3d_{xz}$, with a small admixture of $3d_{yz}$ resulting from distortions of the complex from idealized C_{2v} symmetry, $|\mathrm{SOMO}\rangle = c_1|xz\rangle + c_2|yz\rangle$.[1] The 3d spin density can be computed from $A_\parallel$ and $\langle A\rangle$, using equation (2) where $P = 232 \times 10^{-4}$ $\mathrm{cm^{-1}}$.[14] The

$$A_\parallel - \langle A\rangle = -\tfrac{4}{7}P(c_1^2 + c_2^2) \qquad (2)$$

hybridization ratio, $R = c_2^2/c_1^2$, is computed from the non-coincidence angle α using equation (3). The results for the five-co-ordinate complexes are given in Table 2.

$$\tan\alpha = -2\sqrt{R}/(1 - R) \qquad (3)$$

For the six-co-ordinate complexes we have both a simpler and more difficult problem in estimating the metal contribution to the SOMO. On the one hand the apparent coincidence of the *g* and ^{59}Co hyperfine principal axes suggests that these complexes have symmetries more nearly C_{2v} so that the metal contribution to the SOMO is probably purely d_{xz}. However, we

Table 2 Composition of the singly occupied molecular orbital

Complex	ρ_{3d}	*R*
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2(PPh_3)}]$*	0.31	0.020 ± 0.003
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OPh)_3\}}]$*	0.26	0.009 ± 0.008
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}}]$	0.27	0.025 ± 0.002
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OEt)_3\}}]$	0.27	0.025 ± 0.002
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OBu^n)_3\}}]$	0.28	0.025 ± 0.002
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{PPh(OMe)_2\}}]$	0.29	0.022 ± 0.009
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OPr^i)_3\}}]$	0.28	0.002 ± 0.002
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OCH_2CF_3)_3\}}]$	0.26	0.001 ± 0.002
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{\eta^1\text{-}[(MeO)_2PCH_2]_2\}}]$	0.28	0.028 ± 0.006
$[\mathrm{Co(S_2C_2Ph_2)_2(\eta^1\text{-}dppm)}]$	0.28	0.072 ± 0.020
$[\mathrm{Co(S_2C_2Ph_2)_2(\eta^1\text{-}dppe)}]$	0.27	0.038 ± 0.004
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}_2}]$	0.23	0
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OBu^n)_3\}_2}]$	0.23	0
$[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{PPh(OMe)_2\}_2}]$	0.23	0

* Data from ref. 1.

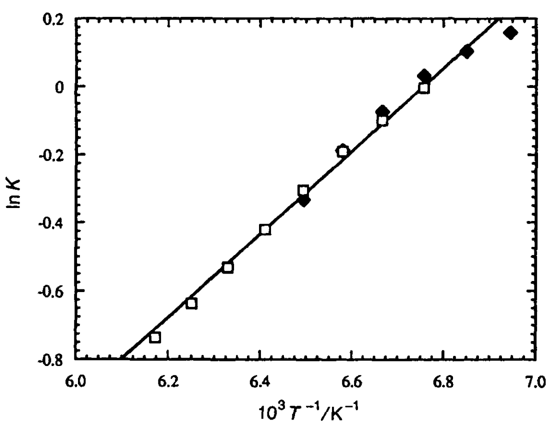

Fig. 3 A van't Hoff plot of equilibrium constants for the addition of $P(OMe)_3$ to $[\mathrm{Co\{S_2C_2(CF_3)_2\}_2\{P(OMe)_3\}}]$. Open symbols refer to *K* determined from the amplitude ratio $A_{6,4}/A_{5,3}$, filled symbols to *K* from $A_{6,8}/A_{5,6}$; the line corresponds to a least-squares fit of the points

need an estimate of $\langle A \rangle$ in order to apply equation (2). In our computer simulations it became apparent that A_x and A_z are small, probably less than 5×10^{-4} cm^{-1}. Assuming $A_x = A_z = (0 \pm 5) \times 10^{-4}$ cm^{-1}, we have, for L = P(OMe)$_3$, $\langle A \rangle = (15.5 \pm 2.4) \times 10^{-4}$ cm^{-1}, $A_{\parallel} - \langle A \rangle = (31.0 \pm 2.5) \times 10^{-4}$ cm^{-1} and $c_1^2 = 0.23 \pm 0.02$. Results for the other six-co-ordinate complexes are given in Table 2.

The ^{31}P coupling constants are consistently larger for the phosphite derivatives than for the phosphines reported earlier, suggesting greater π-back bonding to the phosphites. However, comparing the cobalt 3d spin densities for L = PPh$_3$, PEt$_3$ or P(OPh)$_3$ with those obtained in this work, we see no significant differences, suggesting that π-back bonding makes a very small contribution for the five-co-ordinate complexes. The distortion of the six-co-ordinate complexes, as represented by the angle α or the d-orbital hybridization parameter R, is surprisingly large for the alkyl phosphite ligands, especially when compared with P(OPh)$_3$ or P(OCH$_2$CF$_3$)$_3$. The reason for this difference is not readily apparent.

The 3d spin densities for the six-co-ordinate complexes are substantially smaller than those for the five-co-ordinate complexes. This result, together with the much larger ^{31}P couplings found for the former, points to significant delocalization of the SOMO into π-acceptor orbitals of the phosphite ligands, probably the factor largely responsible for the small, but negative, enthalpy change on addition of the extra ligand. The lack of distortion as measured by the angle α is consistent with the loss of entropy on ligand addition, and both these parameters suggest a highly symmetrical species with significant steric crowding in the co-ordination sphere.

Discussion

Since diffusion in a frozen solution is surely very slow, it is clear that the five-co-ordinate complexes observed in the equilibrium studies are actually solvates with the excess of ligand. The effect of this solvation on the electronic structure of these complexes is apparently minimal, since the ESR parameters are identical to those found from solutions without an excess of the ligand. The observed equilibria thus correspond to the reversible formation of a Co–P bond and the process can be described most succinctly as an outer-sphere/inner-sphere equilibrium. It was somewhat surprising that essentially identical results were obtained using toluene, thf or CH_2Cl_2–1,2-$C_2H_4Cl_2$ as solvent; we had expected that thf solvation would compete with solvation by a phosphite and eliminate or substantially alter the five-/six-co-ordinate equilibrium.

A *trans* stereochemistry is indicated for the six-co-ordinate adducts by a number of arguments: rearrangement to *cis* stereochemistry would be expected to disrupt the metal–dithiolene π interaction which is responsible for the most prominent electronic structure features for these complexes. The components of the g and A^{Co} matrices are qualitatively similar to those of the five-co-ordinate complexes suggesting no major change in stereochemistry. If the metal contribution to the SOMO is d_{xz} (or any other d orbital capable of π interaction with a phosphite ligand), the ^{31}P couplings would have been expected to be non-equivalent for a *cis* isomer. Finally, complexes with L = [(MeO)$_2$PCH$_2$]$_2$, dppm or dppe showed no evidence of chelation.

As in the case of adduct formation by the complexes of VO^{2+} and Cu^{2+} studied earlier,[3,4] the formation of a six-co-ordinate cobalt dithiolene adduct depends on both steric and electronic effects. Thus sterically demanding ligands such as P(OPh)$_3$, P(OPr^i)$_3$ or PPh$_3$ and less basic (or less π-acidic) ligands such as P(OCH$_2$CF$_3$)$_3$ or PEt$_3$ will not add to [Co{S$_2$C$_2$(CF$_3$)$_2$}$_2$L]. When R = CF$_3$ is replaced by a less electron-withdrawing group, Ph, 4-MeC$_6$H$_4$ or 4-MeOC$_6$H$_4$, the six-co-ordinate complex is not formed in frozen solutions, even with P(OMe)$_3$. The thermodynamic parameters obtained in the earlier studies are not strictly comparable with ours since the earlier work involved the bimolecular reaction of two solution species. Nonetheless, it is clear that it involved much stronger Lewis acid–base interactions than observed in the present case. For example, one of the weaker interactions studied was that of copper(II) dibutyldithiocarbamate with pyridine, giving $\Delta H^\circ = -20$ kJ mol^{-1},[7b] twice that observed here.

The ESR spectra assigned to *cis*- and *trans*-[Co(S$_2$C$_2$Ph$_2$)$_2$L$_2$] [L = P(OEt)$_3$, PEt(OEt)$_2$ or PEt$_2$(OEt)] by Yablokov, Ryzhmanova and co-workers[10] were different from those of the *trans* adducts reported here. Spectra assigned to *trans* isomers were obtained at room temperature and showed coupling to two equivalent ^{31}P nuclei with ESR parameters similar to those of the five-co-ordinate complexes; we have seen no such spectra at or below room temperature for any combination of R (CF$_3$, Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$) or L (phosphines, phosphites or phosphonites). The spectra assigned to *cis* isomers were very different with larger g values (≈ 2.07) and cobalt couplings ($\approx 35 \times 10^{-4}$ cm^{-1}) and two very different ^{31}P couplings (≈ 210 and 10×10^{-4} cm^{-1}). Although details were not given, the presumed adducts were formed by reactions either in acetone solution or without solvent and apparently were slow, irreversible, and at temperatures as high as 400 K. It is clear from the present work that the reaction products were not correctly identified and must arise through a more substantial rearrangement than simple addition of a ligand to form a six-co-ordinate complex. We have seen evidence for chemical reactions of cobalt dithiolene complexes with an excess of phosphites and phosphonites on standing at room temperature and have reproduced some of the Russian results. Further work is in progress in an attempt to identify the products.

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