color subsequently observed is indicative of the formation of $Fe_2(CO)_8^{2-}$. On exposure of these solutions to air $[HFe_3(CO)_{11}]^-$ may be formed via the species $[HFe(CO)_4]^-$.

$$3[Fe(CO)_4H]^- \xrightarrow{O_2} [Fe_3(CO)_{11}H]^- + H_2 + CO_3^{2-}$$

Conclusion

The redox behavior of iron carbonyl compounds in basic solvents such as THF is extremely complex and these solvents should be avoided if definitive results are desired. Although the foregoing discussion gives a reasonable picture of the redox behavior of iron cluster compounds in CH_2Cl_2 and THF, there could be other species that have not been characterized. For example, a weak, sharp signal, $g = 2.013$, on which ^{13}C coupling can be recognized, appears in some spectra, especially in those involving photolytic reactions of $Fe_3(CO)_{12}$. A radical anion of a cluster of higher nuclearity? Paramagnetic species may account for only a small percentage of the total present.[41] Nonetheless, they must be considered as possible intermediates in reactions of iron carbonyl compounds in organic solvents and many of the mechanisms postulated for catalysis by $Fe_3(CO)_{12}$ could be questioned. As a corollary, catalysis using $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ may be more efficient using electrolytically reduced solutions. This concept is currently being explored in these laboratories.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the New Zealand Grants Committee for financial support and the University of Otago for the award of a Senior Demonstratorship (to P.A.D.). The interest and helpful advice offered by Professor P. H. Rieger and Dr. D. Watson was appreciated. We also thank Dr. P. Krusic for communicating results prior to publication.

Registry No. $Fe_3(CO)_{12}$, 17685-52-8; $Fe_3(CO)_{11}P(OPh)_3$, 55787-43-4; $Fe_3(CO)_{10}[P(OPh)_3]_2$, 63104-18-7; $Fe_3(CO)_{11}P(OMe)_3$, 63104-15-4; $Fe_3(CO)_{11}PPh_3$, 12101-59-6; $Fe_3(CO)_{10}[P(OMe)_3]_2$, 63104-16-5; $Fe_3(CO)_9[P(OMe)_3]_3$, 63104-17-6; $Fe_2Ru(CO)_{12}$, 20468-34-2; $FeRu_2(CO)_{12}$, 12388-68-0; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; $Fe_2(CO)_9$, 15321-51-4; $[Et_4N][HFe_3(CO)_{11}]$, 55976-22-2; $[Fe_3(CO)_{12}]^{-\cdot}$, 55787-46-7.

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[41] We have found that the majority of polynuclear iron carbonyls when dissolved in basic or protic solvents, and even CH_2Cl_2, under strictly anaerobic conditions will give signals in an ESR spectrum unless the samples are extremely pure. In some instances the signals appear even though oxygen is present (see also ref 31).

Contribution from the University Chemical Laboratory,
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Ligand Field Studies of Phosphine π Acidity and d–s Mixing in *trans*-Dimesitylbis(diethylphenylphosphine)cobalt(II) and Analogues

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The complete paramagnetic susceptibility tensor of crystals of the planar coordinated system *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II) has been measured by the Faraday technique throughout the temperature range 20–300 K. These single-crystal susceptibility data together with the ESR *g* values and solution electronic spectra of the present complex and its analogues when mesityl is replaced by α-methylnaphthyl or pentafluoro- or pentachlorophenyl (reported earlier) have all been quantitatively reproduced within a common theoretical model. The ligand field is parameterized by the angular overlap model, which is unable to account for the energy of the d_{z^2} orbital (where *z* lies perpendicular to the coordination plane), and by an orbital energy parameterization scheme. The results demonstrate (i) a considerable degree of π acceptance by the phosphine ligands, (ii) a marked Naphelauxetic reduction of F_2 and F_4 values, (iii) a depression by several thousand wavenumbers of the d_{z^2} orbital, ascribed to a d–s configurational mixing process, and (iv) a role, by comparisons throughout the series of four complexes, for the hydrogen atoms of the α-methyl groups in the mesityl (and presumably naphthyl) derivatives, which lie close to the central metal, in the d–s mixing process.

Introduction

This study concerns the ligand-field properties of a series of four low-spin, planar-coordinated complexes of cobalt(II). The only member of the series for which an X-ray structure analysis is available[1,2] is *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II), the molecular structure of which is represented in Figure 1. The four-coordinate ligation of the metal atom appears to result from a steric blocking of the potential fifth and sixth sites of an idealized octahedron by the α-methyl groups of the mesityl ligands. A similar rationalization of the stoichiometry, and closely similar electronic properties, serves for the analogous complex in the series in which the mesityl groups are replaced by α-methylnaphthyl ligands. No doubt steric hindrance is less marked in two further analogues in which mesityls are substituted by pentafluoro- or pentachlorophenyl ligands.

An earlier electron spin resonance study,[3] based on single-crystal measurements on the pure mesityl complex and on the cobalt-doped nickel(II) analogue, revealed a rhombic **g** tensor, with principal directions lying close to the axes of Figure 1, which is highly anisotropic with $g_x = 3.72$, $g_y = 1.96$, and $g_z = 1.74$. These *g* values were quantitatively reproduced within a model spanning the strong field, spin-doublet configurations which result without participation of the, presumed high-lying, $d_{x^2-y^2}$ orbital. Admixtures of these configurations into the ground configuration were calculated by using perturbation theory, the final choice of ground level being made by reference to both **g** and hyperfine **A** tensors. It was ultimately dem-

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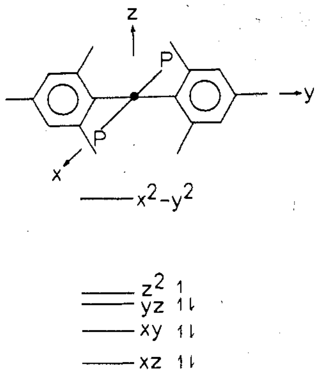

Figure 1. *trans*-Dimesitylbis(diethylphenylphosphine)cobalt(II) coordination geometry and molecular reference frame. Also shown is schematic orbital energy scheme and ground configuration from ref 3.

onstrated that the large g value anisotropy in the molecular xy coordination plane could only be reproduced from an orbital energy ordering scheme in which the yz orbital lies close to the half-filled z^2 orbital while the xz orbital is relatively much more distant, as shown in Figure 1.

Much recent work on the paramagnetism of transition-metal complexes has shown[4] that chemically significant interpretations of ligand field properties are best made within a localized, quasi-valence-bond scheme such as the angular overlap model,[5] and it is only in recent years that a complete theoretical,[6] experimental,[7] and computational[8] system has been developed which enables proper examination of low-symmetry molecules in this way. In the present study we reexamine these low-spin, planar cobalt(II) systems in this spirit. Of particular interest is the π-bonding role of the phosphine ligands in these complexes. Recent studies[9,10] of the magnetic and spectral properties of phosphine-ligated, high-spin complexes of cobalt(II) and nickel(II) have demonstrated a significant degree of π acidity of phosphine ligands: so we may enquire what effect the change from the high-spin to low-spin state of the metal has on this property.

An immediate interpretation of the previously determined configuration energies within the angular overlap model (aom) framework is not satisfactory, however, as some doubt must attach to the energy values found by the limited nature of the early calculations,[3] being based on perturbation theory and a restricted basis. We have therefore reinterpreted the raw experimental data by diagonalization of the complete 120-fold d^7 configurational basis. Further, magnetic susceptibilities reported in the earlier study were limited to the liquid nitrogen temperature range, 80–300 K, and were not accurately determined. This latter was essentially because the large anisotropies meant that measurements using the Krishnan critical torque technique were highly sensitive to small crystal orientation errors, especially those measurements based on crystals not suspended parallel to the (only) symmetry axes in these monoclinic systems. A single-crystal Faraday balance has been described recently[7] which allows these difficulties to be overcome and so we include here detailed measurements of the principal magnetic susceptibilities of the mesityl complex throughout the extended temperature range 20–300 K.

Table I

axis	ξ	η	ζ	$\chi_{max} + \chi_{min}$
[010]	0	1	0	$2\bar{\chi}_{010} = \chi_{aa} + \chi_{c'c'}$
[10$\bar{1}$]	0.6817	0	−0.7317	$2\chi_{10\bar{1}} = 0.535\chi_{aa} + \chi_{bb} + 0.465\chi_{c'c'} + 0.998\chi_{ac'}$
[100]	1	0	0	$2\bar{\chi}_{100} = \chi_{bb} + \chi_{c'c'}$

Experimental Section

trans-Dimesitylbis(diethylphenylphosphine)cobalt(II) was prepared as described in the literature.[11] Large crystals suitable for the measurement of magnetic susceptibility were grown by slow evaporation at −4 °C of a benzene solution over many months. The complex is somewhat unstable in benzene solution with respect to moisture but, once prepared, the crystals are quite stable to air at room temperature.

Susceptibility measurements were made on four crystals weighing 1.5–2.9 mg. The crystals are monoclinic with unit cell dimensions[2] $a = 10.70$ Å, $b = 9.31$ Å, $c = 18.32$ Å, and $\beta = 107.2°$. All crystal orientations were established by X-ray goniometry and measurements were made, by using our single-crystal Faraday balance,[7] for two crystals mounted parallel to b and one each mounted parallel to a and to the [10$\bar{1}$] direction. The two sets of measurements in the ac plane agreed within ca. 3% but the calculations below are based upon those giving the smaller values for the minimum susceptibility in that plane since any orientational error would be expected to increase rather than decrease the observed value.

Values for the principal crystal susceptibilities χ_1, χ_2, and χ_3, where χ_3 lies parallel to b, and for the angle ϕ subtended by χ_1 (defined such that $\chi_1 < \chi_2$) and a, and measured from the positive a axis toward or through the positive c axis, were determined as follows. The average susceptibility in a plane normal to a direction with direction cosines ξ, η, and ζ relative to the orthogonal crystal axes a, b, and c' is given by[12]

$$2\bar{\chi}_{\xi\eta\zeta} = \chi_{max} + \chi_{min} = \chi_{aa}(1 - \xi^2) + \chi_{bb}(1 - \eta^2) + \chi_{c'c'}(1 - \zeta^2) - 2\chi_{ab}\xi\eta - 2\chi_{ac'}\xi\zeta - 2\chi_{bc'}\eta\zeta \quad (1)$$

In this monoclinic system, $\chi_{ab} = \chi_{bc'} = 0$, so using the unit cell dimensions above, we may construct Table I. Further, by inspection, it is observed that χ_{max} for the crystal suspended along [100] corresponds to χ_{bb} ($\equiv\chi_3$). Experimental determinations of both χ_{max} and χ_{min} were made individually in each plane by rotation of the magnet, and the overall crystal anisotropy is evidenced by the appropriate ratio (at 25 K): $\chi_{aa}:\chi_{bb}:\chi_{c'c'} \sim 40:37:15$. The smallest susceptibility $\chi_{c'c'}$ was difficult to measure in these very anisotropic crystals and indeed this was responsible for the reliance placed only on $\bar{\chi}$ and $\Delta\chi_b$ reported in the earlier paper.[3] Values for $\chi_{c'c'}$ observed for crystals mounted parallel to a and b agreed to no better than 10% and the calculations below are based on the a axis measurements which gave the smaller values. Once again the lowest estimate of the minimum susceptibility is considered to reflect the minimum orientational error. Hence, by use of χ_{aa} values from the crystal mounted parallel to b and χ_{bb} and $\chi_{c'c'}$ from that mounted along a, values of $\chi_{ac'}$ were deduced from the mean susceptibility perpendicular to [10$\bar{1}$]. The principal crystal susceptibilities and angle ϕ were then calculated by diagonalization of the χ tensor.

Diamagnetic corrections were made as follows. Each of the four phenyl moieties in the molecule was assigned an anisotropic diamagnetic tensor equal to that reported[13] for benzene such that $K_\parallel{}^D$ perpendicular to the benzene plane is 89×10^{-6} cgsu and $K_\perp{}^D$ in the plane 34×10^{-6} cgsu. The tensor for each fragment was transformed into the orthogonal crystal frame abc' and added to an isotropic molecular diamagnetic tensor of 236×10^{-6} cgsu for the remainder of the molecule computed from Pascal's constants.[14] The same was

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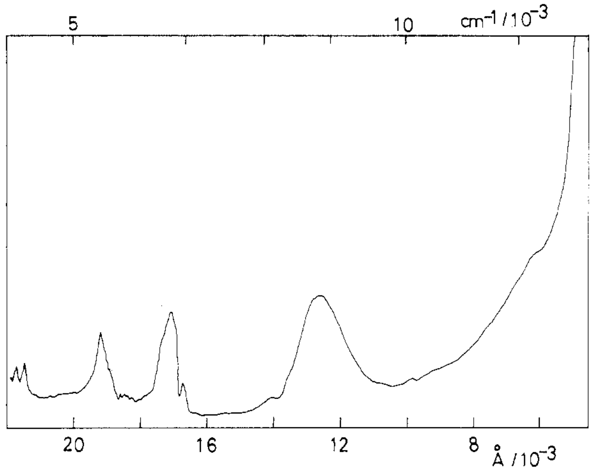

Figure 2. *trans*-Dimesitylbis(diethylphenylphosphine)cobalt(II) electronic spectrum in THF solution. Bands at wavelengths higher than 16 000 Å also appear in the spectrum of the isomorphous nickel(II) analogue. $\epsilon_{\max} \sim 8.5$ for band at 12 500 Å.

repeated for the other molecule in the unit cell and after summing, the total diamagnetic crystal tensor with respect to *abc′* was

$$\begin{array}{c} \\ \chi_1^{\mathrm{D}} \\ \chi_2^{\mathrm{D}} \\ \chi_3^{\mathrm{D}} \end{array} \begin{array}{c} \begin{array}{ccc} a & b & c' \end{array} \\ \begin{pmatrix} 399 & 0 & -38 \\ 0 & 439 & 0 \\ -38 & 0 & 499 \end{pmatrix} \end{array} \times 10^{-6} \text{ cgsu} \qquad \text{(I)}$$

The principal crystal susceptibilities given in Table II are those determined from the measurements and diagonalization, corrected for this diamagnetism.

The spectrum of the complex in tetrahydrofuran solution, redetermined in the near-IR and visible ranges, by using a Cary 14 spectrophotometer, is shown in Figure 2.

Discussion

Basis Functions and Angular Overlap Parameters. All calculations have been performed, by using the theoretical and computational systems described elsewhere,[6,8] within the complete d^7 configuration as basis. Interelectron repulsion, spin–orbit coupling, and orbital-reduction effects in the magnetic moment operators are represented, as usual, by the parameters F_2, F_4, ζ, and k. The ligand field proper was initially considered within the framework of the angular overlap model. While one σ- and two π-bonding parameters may be assigned to each of the two ligand types in the present complex, the nearly perfect rhombic symmetry of the molecule imposes limitations on an effective separation of some of these variables and, in effect, reduces the degree of ligand field parameterization. Thus, by reference to the axis frame of Figure 1, the $d_{x^2-y^2}$ and d_{z^2} orbitals of the central metal atom are affected by σ interaction with both phosphines and mesityls. The σ orbitals on these ligands do not interact with any other metal orbitals, so that there is no possibility, within the idealized rhombic (or D_{2h}) symmetry of the coordination shell, of distinguishing the σ-bonding roles of the different ligands. Accordingly, we represent their average σ interaction by the aom parameter e_σ(av). The mesityl ligands are oriented almost exactly perpendicular to the plane of the donor atoms so that π interaction with the cobalt atom, represented by $e_{\pi\perp}$(M), should affect only the d_{xy} orbital. We presume that there is no π bonding between the metal and the mesityls in the plane of these ligands and so take $e_{\pi\parallel}(\mathrm{M}) = 0$: we discuss this assumption later. We represent the π interaction of the phosphine ligands by the single parameter e_π(P), even though each phosphorus atom is unsymmetrically coordinated to two ethyl and one phenyl groups. No essential restriction is implied here, however, as any anisotropy in phosphine π bonding is inseparable from the mesityl $\pi_\perp$ bonding. Thus, if we resolve the phosphine π bonding parallel and perpendicular to the metal coordination plane (xy)—which is geometrically a reasonable approximation to the local pseudosymmetry of the phosphine groups—$e_{\pi\parallel}$(P) relates to the metal d_{xz} orbital and $e_{\pi\perp}$(P) to d_{xy}. Hence any error involved in the assumption of axially symmetric metal–phosphine π interaction is parametrically taken up in a false value for $e_{\pi\perp}$(M). Altogether, therefore, the aom parameter list in the present complex comprises e_σ(av), e_π(P), $e_{\pi\perp}$(M) (and $e_{\pi\parallel}$(M), expected to be zero).

Table II. Co(mesityl)$_2$(PEt$_2$Ph)$_2$ Observed Principal Crystal Susceptibilities, Interpolated and Corrected for Diamagnetism from Equation I[a]

T/K	χ_1	χ_2	$\chi_3 = \chi_b$	$\bar{\chi}$	ϕ/deg
20	1730	3890	3800	3140	91
25	1430	3210	3190	2610	94
35	1020	2330	2300	1880	92
45	786	1820	1800	1470	94
55	663	1510	1510	1230	96
65	556	1300	1270	1040	96
75	463	1170	1110	913	97
85	397	1050	976	808	97
95	359	936	874	723	96
105	326	845	793	655	97
115	301	778	732	604	97
125	280	720	679	559	97
135	262	669	631	521	97
145	246	625	591	487	97
155	233	587	558	459	97
165	221	554	530	435	97
175	210	526	504	413	97
185	201	501	480	394	97
195	193	476	458	376	97
205	185	454	439	360	98
215	179	436	421	345	97
225	173	418	405	332	97
235	167	399	390	319	97
245	161	382	377	307	98
255	157	370	364	297	97
265	154	361	352	289	96
275	150	348	342	280	97
285	146	334	332	271	97
295	142	324	322	263	96

[a] Values given in cgsu $\times 10^{-5}$ (1 cgsu $= 4\pi \times 10^{-6}$ m^3 mol^{-1}).

Note that, within the idealization of rhombic coordination symmetry the d_{yz} orbital of the metal is unaffected by the ligand field: only in-plane π bonding from the mesityl groups could affect the energy of d_{yz}. *Hence all other d orbital energies can be considered as shifted with respect to* d_{yz}. Now in rhombic symmetry, the energies of the $x^2 - y^2$ and z^2 orbitals are given directly as $3e_\sigma$(av) and e_σ(av), respectively. The earlier[3] perturbation and basis-limited calculations placed the z^2 orbital only about 1000 cm^{-1} above the yz. A value for e_σ(av) of ca. 1000 cm^{-1}, so implied, is unacceptable. We ask, therefore, whether the same result emerges from the present full-basis diagonalization.

By the variation of e_σ(av) in the range 4000–7000 cm^{-1}, e_π(P) in the range 4000 to −5000 cm^{-1}, and $e_{\pi\perp}$(M) from 0 to 4000 cm^{-1}, together with wide variations of F_2 and F_4, fair agreement with the crystal susceptibilities is sometimes possible but no acceptable reproduction of the molecular g values is achieved. Typical of these calculations is the set $g_1 = 2.1$, $g_2 = 2.4$, $g_3 = 2.7$, at best, no g value calculating greater than ca. 2.8, let alone 3.7 as found experimentally for g_x. The eigenvalues corresponding to all these calculations are never characterized by a close energetic approach of the yz and z^2 levels. The conclusions of the earlier theoretical treatment thus have qualitative support. The central factor in the reproduction of the ligand field properties of this complex is, therefore, the

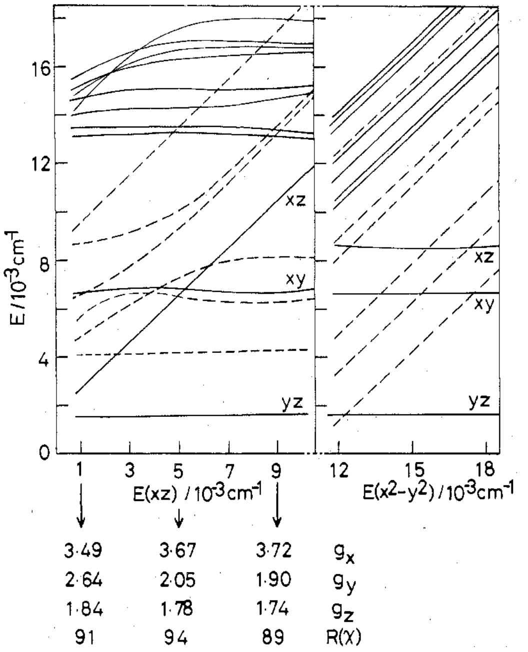

Figure 3. Term energies calculated within complete d^7 basis, for parameters $E(yz) = 0$, $E(z^2) = 500$, $E(xy) = -2000$, $F_2 = 600$, $F_4 = 75$, and $\zeta = 525$ cm^{-1} and shown as functions of $E(xz)$ (a) for $E(x^2 - y^2) = 15\,000$ cm^{-1} and of $E(x^2 - y^2)$ (b) for $E(xz) = -7000$ cm^{-1}. All term energies are plotted with respect to the ground doublet (transforming as z^2): spin doublets shown as solid curves, quartets as broken lines. The diagrams are complete up to ca. 16 000 cm^{-1}. The lowest spin doublets are labeled according to the principal orbital which is half-filled. In (a) principal g values are calculated to lie within 2° of the frame shown in Figure 1. Values of $R(\chi)$ (ref 6 and 8) express approximate agreement with all observed susceptibilities over the 25–300 K temperature range.

energy of the z^2 orbital relative to the yz. Except by raising the energy of the d_{yz} orbital by a significant degree of donation in the plane of the mesityl ligands, which we consider quite unreasonable, the aom is unable to reproduce the observed properties.

Orbital Energy Model. The successful application of the aom scheme to the ligand field properties of so many other[4] systems strongly suggests that the present failure is concerned specifically with the energy placing of the d_{z^2} orbital alone. We shall argue that the present system involves a degree of mixing between 3d and 4s metal functions, as proposed in several other systems,[15–18] but first we establish the magnitude of the effect we wish to explain. For this, it is convenient to use an orbital energy parameterization scheme in which the molecular symmetry is idealized to D_{2h}. This has the further advantage of fitting the energies of the xz and xy orbitals independently and without any "working prejudice" about the degree of anisotropy in metal–phosphine π bonding. Ultimately, we relax this restriction of D_{2h} coordination symmetry and allow for the small nonrhombic distortions in the coordination shell. Meanwhile, we refer to the parameters $E(x^2 - y^2)$, $E(z^2)$, $E(yz)$, $E(xy)$, and $E(xz)$, describing the energies of the individual real d orbitals. All 120 term energies are calculated from these values by the usual vector coupling techniques. In D_{2h} symmetry, a matrix element exists to mix $d_{x^2-y^2}$ and d_{z^2} functions; however, as the $x^2 - y^2$ orbital lies at much higher energy than z^2, we set this off-diagonal term to zero and regard $E(z^2)$ and $E(x^2 - y^2)$ as diagonalized energies for the *pure* z^2 and $x^2 - y^2$ functions. As the present scheme is ultimately checked against one without D_{2h} restrictions, no serious error is so involved. Altogether, therefore, our second model is parameterized by these five orbital energies together with F_2, F_4, ζ, and k.

Table III

	obsd	calcd	orientation with respect to *a*, *b*, *c*′ obsd	orientation with respect to *a*, *b*, *c*′ calcd
g_x	3.72	3.72	42.0, 48.1, 88.2	43.7, 46.7, 85.6
g_y	1.96	1.99	129.6, 46.0, 70.5	131.3, 49.2, 68.3
g_z	1.74	1.76	78.4, 105.6, 19.7	78.2, 108.5, 22.2

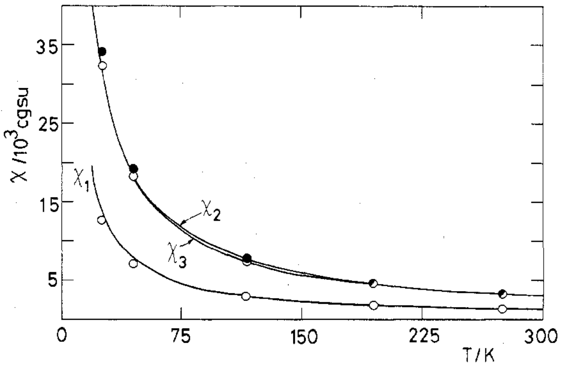

Figure 4. *trans*-Dimesitylbis(diethylphenylphosphine)cobalt(II): comparison between observed principal crystal susceptibilities and those calculated (circles) by using parameters II.

Reproduction of Spectrum, Susceptibilities and g Values. After several preliminary calculations in which all parameters were varied freely, three main issues emerge: (a) The interelectron repulsion parameters are of concern as they help establish the required spin-doublet ground state. We require a large value for $E(x^2 - y^2)$ and rather low ones for F_2 and F_4. (b) The largest g value of 3.7 is reproduced only by calculations in which the z^2 orbital lies well within 1000 cm^{-1} of the yz orbital, confirming the earlier calculations. (c) The overall **g** tensor, crystal susceptibilities, and optical spectrum are reproduced only if the xz orbital lies several thousand wavenumbers below the yz, implying a considerable π accepting role for the phosphine ligands.

Figure 3 shows the variation of term energies, g values and susceptibility agreement factors with respect to $E(xz)$ and $E(x^2 - y^2)$. The effects of variations of these two orbital energies are essentially independent. The spectral features at ca. 8000 cm^{-1} may be assigned to transitions involving the transfer of a hole from the z^2 orbital to the xy and xz, that is, in the strong-field limit from $(xz)^2(xy)^2(yz)^2(z^2)^1$ to $(xz)^1(xy)^2(yz)^2(z^2)^2$ and $(xz)^2(xy)^1(yz)^2(z^2)^2$, respectively. We assign both transitions to the main spectral peak at 8000 cm^{-1} or, alternatively, to that peak and the small shoulder at ca. 7500 cm^{-1}. Apart from peaks at lower energies which also appear in the spectrum of the nickel(II) analogue, the spectrum is essentially featureless except for a small shoulder at ca. 16000 cm^{-1} on what we presume is the tail of a charge-transfer spectrum above 20 000 cm^{-1}. Parts a and b of Figure 3 show that changing $E(x^2 - y^2)$ from 15 000 to 18 000 cm^{-1} ensures that no other spin-allowed (doublet) transitions are calculated to lie between 8000 and 16000 cm^{-1}. The paucity of spectral information in that region, however, limits confidence in a value for $E(x^2 - y^2)$ on these grounds alone.

The assignment of the xz transforming level at ca. 8000 cm^{-1} is also supported by the calculated g values and crystal susceptibilities, as indicated below Figure 3. There is not a 1:1

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Table IV. $Co(mesityl)_2(PEt_2Ph)_2$ Calculated Energy Levels in Wavenumbers, for Parameter Set II[a]

0, 1683, 7073, *7162,* 8030, *9593, 11 120, 13 512, 14 220,*
16 162, 16 417, 17 343, *18 017,* 18 396, 19 442,
19 986, 20 254, 21 190, 22 846, 23 534, 23 644,
24 499, 26 649, 27 289, 27 841, *27 868, 33 773,*
33 792, 34 490, 36 575, 36 729, 36 805, 37 385,
37 762, 37 944, 41 159, 42 008, 42 410, 42 481,
42 710, 43 380, 43 527, 43 932, 44 528, 44 777,
45 305, 54 371, 54 790, 55 930, 56 029

[a] Quartets (averaged over multiplet) in italics, doublets in roman type. Observed spectral maxima at ca. 8000 cm^{-1}, ca. 7500 cm^{-1} (shoulder).

correspondence between the parametric orbital energies and the calculated term energies but, by interpolation of the data in Figure 3, together with calculations in which $E(z^2)$ was varied from −500 to +1000 cm^{-1} in steps of 100 cm^{-1}, we established the following parameter set which satisfactorily reproduced the magnitudes and orientations of the principal g values and susceptibilities:

$$\begin{array}{c} E(z^2) = 500\ \text{cm}^{-1} \qquad E(x^2 - y^2) = 18\,000\ \text{cm}^{-1} \\ E(xz) = -6400\ \text{cm}^{-1} \qquad E(xy) = -2400\ \text{cm}^{-1} \\ E(yz) = 0 \qquad \zeta = 515\ \text{cm}^{-1} \qquad F_2 = 600\ \text{cm}^{-1} \\ F_4 = 75\ \text{cm}^{-1} \qquad k = 0.93 \end{array} \tag{II}$$

The agreement between observed and calculated quantities is represented: (i) by Table III, (ii) by observed and calculated principal crystal susceptibilities agreeing within 6% over the 25–300 K temperature range as shown in Figure 4, and (iii) by the calculated energy levels, in Table IV, reproducing the observed spectral features.

The earlier, limited theoretical treatment suggests that ζ was reduced from the free-ion value by, say, 25%, for an energy separation $z^2 - yz$ of ca. 1000 cm^{-1} (or no reduction for $\Delta E \sim 1300\ cm^{-1}$) while the present calculation gives $\zeta \sim \zeta_0$ and $E(z^2) - E(yz) = 500\ cm^{-1} \pm 100\ cm^{-1}$. Similarly, in the present model an orbital energy separation $z^2 - xz$ of 6900 cm^{-1} is manifest in the corresponding term separation of ca. 8000 cm^{-1}. These features both illustrate the, perhaps surprisingly small, differences between the restricted-basis with perturbation-theory model and the diagonalization of the complete 120-fold, d^7 configurational basis. Larger differences occur with somewhat different parameter values, however, as discussed later.

Nephelauxetic Effects. A very large nephelauxetic effect is evident in the low F_2 and F_4 values. Free-ion values for Co^{2+}, are $B_0 = 1120\ cm^{-1}$ with $C_0/B_0 = 3.9$ or, equivalently, $F_2 = 1745$ and $F_4 = 125\ cm^{-1}$, as compared with respective values of 600 and 75 cm^{-1} here. With the same orbital energy parameters as above, larger interelectron repulsion parameters yield a spin-quartet ground term and no agreement with observed properties. By use of smaller ligand field parameter values, even smaller F_2 and F_4 values are required to ensure a spin-doublet ground term. The reproduction of a spin-doublet ground term is achieved by raising the energy of the $x^2 - y^2$ orbital. When $E(x^2 - y^2) = 24\,000\ cm^{-1}$, corresponding to $e_\sigma(\text{av}) = 8000\ cm^{-1}$, good fit to observed g values requires slightly lower values of $E(z^2)$ with the higher $E(x^2 - y^2)$ energy, an energy between 100 and 300 cm^{-1} being optimal. Other ligand field parameters remain unchanged from the earlier set. There is a strong correlation with F_2 and F_4, as expected, best agreement with g values and susceptibilities being found for $F_2 = 950$ and $F_4 = 120\ cm^{-1}$. Even higher values of $E(x^2 - y^2)$ require $F_4 > F_4$ (free ion) which, though not impossible, suggests that $E(x^2 - y^2) \leq 24\,000$; that is $e_\sigma(\text{av}) \leq 8000\ cm^{-1}$. This limit is further supported by noting that the agreement with the g values is somewhat less good for the higher value of $E(x^2 - y^2)$ than for 18000 cm^{-1}, the best obtainable being for $k = 0.95$ when $g_x = 3.70$, $g_y = 2.01$, and $g_z = 1.78$. The susceptibilities do not establish $E(x^2 - y^2)$ within this range, and, once more, best agreement with the spectrum occurs for $E(xz) = -6400\ cm^{-1}$ though satisfactory reproduction of the paramagnetism is obtained for $E(xz)$ in the range −5000 to −8000 cm^{-1}. The correlation between interelectron repulsion parameters and the energy of the $x^2 - y^2$ orbital may be summarized as follows:

$E(x^2 - y^2)$	18 000 cm^{-1}	24 000 cm^{-1}
F_2/F_2(free ion)	0.35	0.55
F_4/F_4(free ion)	0.60	0.96
B/B(free ion)	0.20	0.31

Although values for F_2 and F_4 cannot be established precisely, there is undoubtedly a large nephelauxetic effect in the present complex. This result may be compared with that found in similar studies[9,10] of $Co(PPh_3)_2Cl_2$ and $Co(PPhEt_2)_2Cl_2$, both involving the cobalt(II) atom in the high-spin form. Even in these nominally tetrahedral complexes a large nephelauxetic effect was observed such that $B/B_0 \sim 0.5$. That the reduction in B in the present system is even greater does not follow *directly* from the low-spin state of the metal atom as that might be expected to involve greater electron crowding and so increase rather than decrease interelectron repulsion parameters. However, the Co–P bond length in the mesityl system[2] is 2.24 Å as compared with 2.37 Å in the corresponding $Co(PPhEt_2)_2Cl_2$ molecule[10] and correlation between increased nephelauxetic effects and shorter bond lengths have been observed before.[19]

We interpret the large reduction in interelectron repulsion effects in terms of the space available to the spectral electrons being increased by virtue of the π-accepting role of the phosphine ligands, as argued recently[9] for the series of complexes $M(PPh_3)_2X_2$ where M = Co(II) or Ni(II) and X = Cl or Br. In the present system, the evidence for a significant π-acceptor role for the phosphine ligands derives from the energy of the xz orbital, established at ca. −6400 cm^{-1} relative to yz. Within strict D_{2h} symmetry, this corresponds to a value for $e_{\pi\perp}(\text{P}) = -3200\ cm^{-1}$, any possible anisotropy in the π-bonding role of the phosphines being inseparable from the $\pi_\perp$ role of the mesityl groups as discussed earlier. This value is considerably larger than that estimated in $Co(PPh_3)_2Cl_2$, where $e_\pi(\text{P}) \sim -1000$ to 2000 cm^{-1}. On the other hand, the σ bonding parameter $e_\sigma(\text{av})$ (which is, of course, a mean value for mesityl and phosphine ligands) probably lies in the range 6000–8000 cm^{-1}. Thus $PPhEt_2$ appears to act at least as well as a π acid in the low-spin complex as PPh_3 does in the high-spin system. We conclude, in both high-spin and low-spin systems, that there exists a strong correlation between a large π-acceptor role for the phosphines and a large nephelauxetic effect.

d–s Configuration Mixing. This system appears to be the latest of an increasing number of planar or near-planar coordinated transition-metal complexes directly or indirectly revealing an "anomalous" z^2 orbital energy. In D_{4h} symmetry, representative of many regular square-planar complex geometries, metal 4s and $3d_{z^2}$ orbitals both transform as a_{1g} and can mix, with the result that the d_{z^2} orbital will be stabilized with respect to any other effects represented within a pure d-orbital basis. No such mixing occurs in strict O_h symmetry, of course, and in that the extent of mixing must be associated with the different effective potentials parallel and perpendicular to the symmetry plane in tetragonally distorted octahedra and square-planar systems and related, no doubt, to the difference in metal–ligand overlap in these directions, it is to be expected

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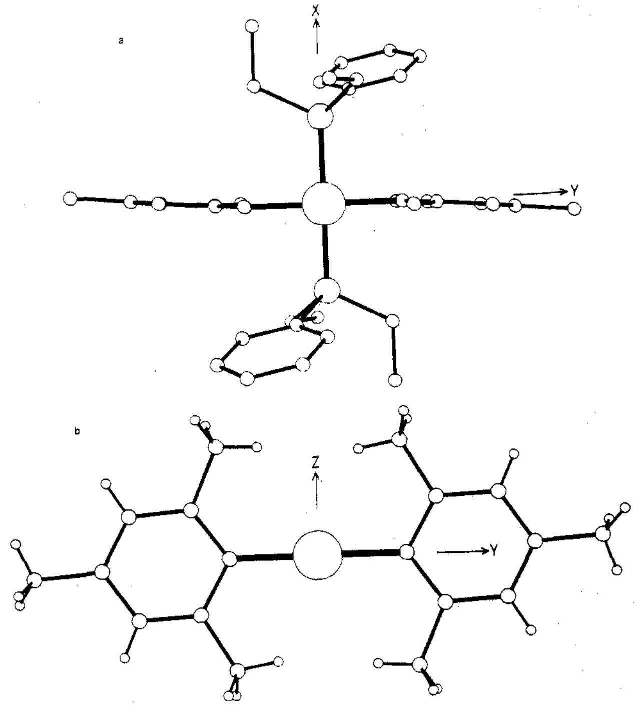

Figure 5. Small distortions in the coordination geometry of *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II): (a) showing non-coplanarity of the mesityl groups, the planes of which lie 0.324 Å apart, and (b) showing unequal Co···H contacts, associated with "misdirected valency" of mesityl σ interaction with the central metal.

that the effect will be greatest in the most "distorted" or planar geometries. The effect, which represents a limitation of the simple angular overlap model, has been proposed to account for anomalies in the spectra of several copper(II) complexes[15] and of planar nickel(II) diamine systems[16] and has received more direct support from the isotropic hyperfine coupling constants of some planar cobalt(II) molecules.[17] Indeed the earlier ESR study[3] of the present mesityl complex also required an estimated 5% admixture of 4s electron density into the $3d_{z^2}$ function in order to account for the magnitude and sign of the observed hyperfine coupling constant. A recent study[18] of gillespite, a mineral containing planar four-coordinate high-spin iron(II), has also provided strong evidence for such $4s$–$3d_{z^2}$ mixing. The magnitudes of the depression of the d_{z^2} energy proposed in several of these investigations are of the order 5000–6000 cm^{-1}. A similar shift is implied in the present study, for if $e_\sigma(av)$ is, say, 6000 cm^{-1}, the stabilization due to d–s mixing is required to be ca. 5500 cm^{-1}. Of course, a closer idealization of the symmetry in the mesityl complex is D_{2h}, under which point group s, d_{z^2}, and $d_{x^2-y^2}$ all transform as a_g, so we might also consider some stabilization of the $x^2 - y^2$ orbital by the same process. However, the rhombic component of the "distortion" from an octahedral precursor is obviously much less than the tetragonal component, so we would guess that the effect of d–s mixing would be very small. In any case we cannot demonstrate such an effect which would be intimately bound up with the aom parameterization in $e_\sigma(av)$. By contrast, the "anomalous" energy of the z^2 orbital is well established in the present study.

Verification of the "Anomalous" Energy of the z^2 Orbital. Within the orbital energy model, the neglect of the off-diagonal matrix element between d_{z^2} and $d_{x^2-y^2}$ serves to overestimate $e_\sigma(av)$. Overall, the depression of the z^2 orbital energy below that determined by the aom is somewhat less than suggested by the simple model we have adopted. We expect the error to be small in view of the large energy separation between z^2 and $x^2 - y^2$ orbitals but the small $z^2 - yz$ separation is still established by the g value and susceptibility anisotropies.

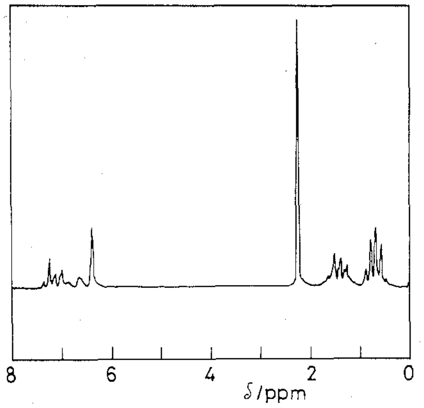

Figure 6. *trans*-Dimesitylbis(diethylphenylphosphine)nickel(II) proton NMR spectrum (100 MHz).

Central to this discussion is that the z^2 orbital lies at an anomalously low energy rather than that the yz orbital, 500 cm^{-1} below it, lies at an anomalously high one. From the minor coordination distortions shown in Figure 5, we expect that the mesityl σ donor orbital is somewhat misdirected with respect to the C–Co axis. However, the deviation of the metal atom from the idealized mesityl diad is so small that a shift of some 5000 cm^{-1} in d_{yz} due to interaction with the mesityl σ orbital would require a value for $e_\sigma(M)$ in excess of 20 000 cm^{-1}. A similar shift in d_{yz} from in-plane Co–mesityl π bonding, directly, is also unacceptable.

A further possibility is to consider the direct ligand field influence of the nearby hydrogen atoms of the α-methyl groups on the mesityl ligands. A recent X-ray refinement of this structure locates two pairs of methyl hydrogens at 2.56 and 2.79 Å from the cobalt atom, as shown in Figure 5b. Metal–hydrogen interactions in these circumstances have been proposed, for example by Cotton[20] in (diethyl-1-pyrazolylborato)(η^3-phenylallyl)(dicarbonyl)molybdenum and by Mason[21] in *trans*-diiodobis(dimethylphenylphosphine)palladium(II), their arguments being based on the close approach of the hydrogen atoms as evidenced by X-ray structural studies (2.27 and 2.8 Å for these two cases, respectively). The methyl proton NMR of the isomorphous, diamagnetic nickel(II) analogue of the present system is shown in Figure 6. Somewhat surprisingly, whether or not the α-methyl hydrogens are involved in weak binding to the metal atom (and this need not be the same in both cobalt and nickel complexes, differing in their complements of d_{z^2} electrons), the chemical shifts of all nine protons, or all three methyl groups, are essentially equal. Shaw[22] has reported a similar result in some related systems.

The direct ligand-field effect of placing partially positively charged hydrogen atoms at sites determined by the X-ray refinement[2] is to stabilize both d_{z^2} and d_{yz} but the latter relatively more. The anomalously close energetic approach of these two orbitals, therefore, is not ascribable to a direct crystal field effect of the nearby hydrogen atoms. It is true, however, that the taking of $E(yz)$ as a zero-energy reference ignores any such contribution from these blocking hydrogens and their neglect bears upon subsequent estimates of all aom parameters: the errors so introduced are surely small and the semiquantitative nature of our conclusions is quite unchanged.

A Role for the Blocking Hydrogen Atoms in the d–s Mixing Process. We return, therefore, to the belief that the anomalous

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Table V. Observed and Calculated Principal g Values for the Series $Co(PEt_2Ph)_2L_2$[a]

	L = mesityl		L = α-methyl-naphthyl		$L = C_6F_5$		$L = C_6Cl_5$	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
g_x	3.72	3.72	3.72	3.72	3.19	3.22	2.76	2.76
g_y	1.96	1.99	2.04	1.99	2.36	2.20	2.42	2.23
g_z	1.74	1.76	1.72	1.76	1.90	1.91	1.95	1.97
$E(z^2)/cm^{-1}$	500		500		1500		3000	

[a] Calculated g values correspond to parameter set II except for $E(z^2)$. Best fits are obtained when $E(xz)$ is also changed; see text.

$z^2 - yz$ energy gap owes nothing to an energetically elevated yz orbital and that, as taken at the outset, the yz orbital may be taken as an approximately zero energy reference. We take the view that d–s mixing is responsible for the low z^2 energy but, in comparing the effect along an analogous series of complexes, argue that the blocking hydrogen atoms are not innocent in the configuration mixing process.

The earlier ESR study[3] reported g values for three analogues of the mesityl complex which are presumed isostructural, though not isomorphous. All four complexes have the formula $Co(PPhEt_2)_2L_2$ where L = mesityl, α-methylnaphthyl, and pentafluoro- and pentachlorophenyl and the principal g values are given in Table V.

The similar g values of the mesityl and α-methylnaphthyl complexes correlate with the presence of α-methyl blocking groups in the fifth and sixth coordination sites of the idealized cobalt octahedron: we presume that similar close cobalt–hydrogen contacts obtain in the α-methylnaphthyl derivative. Steric hindrance is no doubt less in the halophenyl systems but note that the **g** tensors do not change in the order expected just on the grounds of ligand bulk. The possibility exists, therefore, that the close hydrogens in both mesityl and α-methylnaphthyl complexes may contribute to the ligand field properties in an *indirect* way by augmenting the potential under which d–s mixing takes place. In effect, the presence of partly positive groups along or near the z axis takes the ligand field beyond the planar situation normally supposed to be the ultimate tetragonal distortion of an octahedron.

We have therefore attempted to reproduce the observed g values throughout this series of complexes by using the same parameter set (II) as for the mesityl complex except for $E(z^2)$. The overall fits, optimized for $E(z^2)$ = 500, 300, 1500, and 3000 cm^{-1} for mesityl through chloro derivatives, respectively, are shown in Table V. More precise agreement, within ±0.03 for all g values, is only achieved, however, for a simultaneous variation in $E(xz)$, optimal values for which are −6400, −6400, −3500, and −2500 cm^{-1}, respectively; in each case the quality of fit is insensitive to variations of ±1000 cm^{-1} in these energy values. We interpret this trend of decreasing π acidity of the phosphine ligands when methyl groups on the aryl ligands are replaced by halogens as reflecting a reducing donor property of the central metal atom following a decreasing σ donation from the halophenyl groups relative to the mesityl and α-methylnaphthyl derivatives. Accordingly, we have examined the effect of decreasing e_σ(av) [which may involve an increased e_σ(P) outweighed by decreased e_σ(aryl)] upon g values and electronic spectra.

Variation of e_σ(av) in the range 10 000–20 000 cm^{-1} affects g values insignificantly. The effect on the energy spectrum, however, is more important and is shown in Figure 7 for the case $E(xz) = -2500$, $E(z^2) = 3000$ cm^{-1}, corresponding to the pentachloro derivative. The energetically lowest nine spin-doublet levels are shown, labeled according to the principal orbital which is half-filled. In this region of parameter space, close agreement between orbital and term energies does not obtain, illustrating the limitations of the earlier doublet configuration model as compared with the present complete d^7-based calculations. In particular, while the xy and xz orbitals are placed within 500 cm^{-1} of each other, the corresponding states are separated by up to 3000 cm^{-1}. A similar raising of the xy-transforming term is evident also in Figure 3. The absorption spectra of all four complexes are similar,[3] in that only one feature has been reported at lower energy than the charge-transfer tail (other than bands also found in the nickel derivatives). In the mesityl complex, this band maximum occurs at ca. 8200 cm^{-1}: in the naphthyl, fluorophenyl, and chlorophenyl derivatives, maxima occur at ca. 8200, 9450, and 10 900 cm^{-1}. From Figure 7, therefore, we assign the transitions $(xz)^2(xy)^2(yz)^2(z^2)^1 \rightarrow (xz)^2(xy)^1(yz)^2(z^2)^2$ and $\rightarrow (xz)^2(xy)^2(yz)^2(x^2-y^2)^1$ to the same broad feature around 10 900 cm^{-1} and estimate $E(x^2 - y^2)$ as ca. 15 000 cm^{-1}.

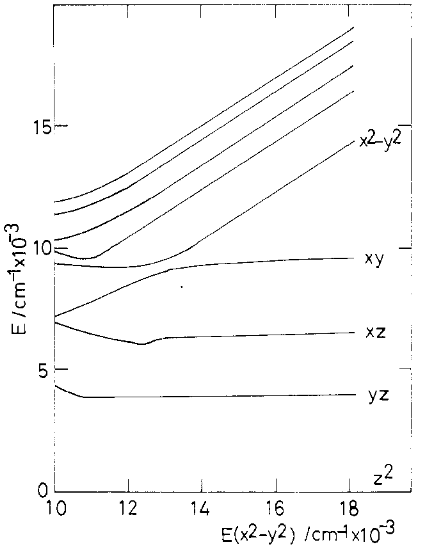

Figure 7. Energies of nine lowest spin doublets, calculated as functions of $E(x^2 - y^2)$ for parameter set II but with $E(xz) = -2500$, $E(z^2) = 3000$ cm^{-1}.

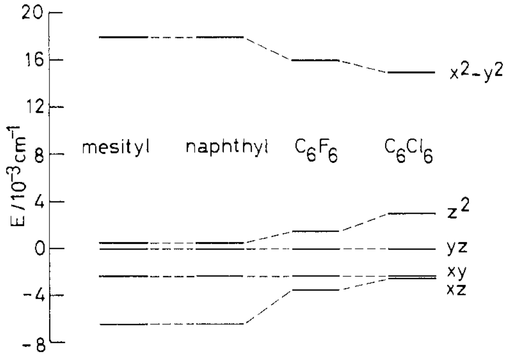

Figure 8. Comparison of "best-fit" orbital energies for the series *trans*-$Co(PPhEt_2)_2L_2$.

A smaller e_σ value for the halophenyl ligands compared with mesityl and α-methylnaphthyl implies a lower energy for the z^2 orbital as calculated from the aom scheme. That $E(z^2)$ values, found by fitting the g values, *increase* (from 500 to 3000 cm^{-1}) despite this trend argues strongly for a decreasing role for d–s mixing on replacing mesityl by pentachlorophenyl groups. The present study, therefore, appears to indicate an indirect role for the blocking hydrogen atoms in the mesityl (and α-methylnaphthyl) complex in augmenting the extent of d–s mixing. Further support for this derives from the numerically smaller values of the Fermi contact parameter for the chloro complex as compared with those of the mesityl compound, previously derived[3] from the ESR hyperfine coupling tensors.

Conclusions

The complete single-crystal ESR and susceptibility tensors of this series of four low-spin, planar cobalt(II) complexes, together with solution absorption spectra in the near-IR and visible regions have been reported in this and the earlier paper.[3] All data have been quantitatively reproduced within a common framework, the ligand field being parameterized within an orbital energy scheme appropriate to D_{2h} symmetry, or the angular overlap model in the true geometry augmented by a stabilization of the d_{z^2} function by interaction with a metal s function.

Approximate orbital diagrams throughout the series are compared in Figure 8. The theoretical treatment of the results, while qualitatively confirming the conclusions of the earlier doublet-restricted model, indicates the need for the present complete d^7 configurational basis, especially with respect to our conclusions relating to the nephelauxetic effect and to trends along the series of particular concern to the role of the α-methyl hydrogen blocking groups. The conclusions of central chemical concern are (i) the π-acid role of the phosphine ligands in these systems, possibly via $d\pi$–$d\pi$ bonding, evidenced by both aom e_π parameters and a much enhanced nephelauxetic effect, (ii) the extent of d–s configurational mixing in the system, depressing the d_{z^2} orbital by several thousand wavenumbers, and (iii) the indication of an indirect role for the blocking hydrogen atoms, in the mesityl and α-methylnaphthyl derivatives, in augmenting the d–s mixing process.

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Registry No. $Co(PEt_2Ph)_2(mesityl)_2$, 22622-24-8; $Co(PEt_2Ph)_2$(α-methylnaphthyl)$_2$, 30975-77-0; $Co(PEt_2Ph)_2(C_6F_5)_2$, 31116-45-7; $Co(PEt_2Ph)_2(C_6Cl_5)_2$, 22638-77-3.

Contribution from Ames Laboratory—USDOE and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Comparative Mass Spectrometry of the Group 6B Hexacarbonyls and Pentacarbonyl Thiocarbonyls

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Mass spectra, ionization energies, fragmentation energies, ionic and neutral dissociation energies, and heats of formation for the title compounds are measured and compared. Substitution of CS for CO in going from $M(CO)_6$ to $M(CO)_5CS$ results in (a) a slight modification of the mass spectra, if only the $M(CO)_nCS^+$ and M^+ ions are considered, (b) a lowering of the ionization energies by 0.1–0.4 eV, (c) a reduction of approximately 0.1 eV in the average M–CO bond energies in both the molecule and the molecular ion, and (d) a reduction of 3.0 ± 0.3 eV in the heats of formation of the molecules. Within each molecule or molecular ion the M–CS bond is stronger than the M–CO bonds by 1.5–2.0 eV. Both the M–CS and the M–CO bonds increase in strength in going from Cr to Mo to W. Comparison of calorimetric and mass spectrometric data for $M(CO)_6$ indicates that each neutral CO fragment leaves the ionization site in its first vibrationally excited state.

Introduction

During the past decade there has been considerable experimental and theoretical interest in transition-metal thiocarbonyl complexes.[1-3] Particular emphasis has been placed upon comparing the strengths of the M–CO and M–CS bonds. As a result the group 6B metal pentacarbonyl thiocarbonyls, $M(CO)_5CS$, have received much attention recently. The preparation and chemistry of these compounds have been described.[4-7] These studies reveal that CS forms a more stable M–C bond than does CO, activates the metal atom toward CO substitution (particularly in the trans position), and undergoes electrophilic addition and nucleophilic attack more readily than does CO. These conclusions are supported by matrix isolation studies,[8,9] studies of vibrational spectra,[10] and theoretical calculations.[11,12]

In this paper we report the mass spectra, ionization energies, and heats of formation of the group 6B hexacarbonyls and pentacarbonyl thiocarbonyls. We also compare quantitatively the M–CO and M–CS bond energies in the pentacarbonyl thiocarbonyls. In the remainder of this paper, pentacarbonyl thiocarbonyl will be shortened to thiocarbonyl.

Experimental Section

The metal carbonyls were obtained from Alfa Inorganics, Inc., Beverly, MA, and were used without further purification. The thiocarbonyls were kindly provided by B. D. Dombek (Iowa State University, Ames, IA). Hexacarbonyl impurities in the chromium and tungsten thiocarbonyls were removed via preparative gas chromatography[4] to yield a product >99.9% pure. The molybdenum compound is not sufficiently stable to be purified by this method and was used without further purification. The presence of 30–40% $Mo(CO)_6$ impurity precluded obtaining experimental data for $Mo(CO)_n^+$ (n = 0–5).

The mass spectrometer used for this research has been described previously.[13] The instrument consists of two 15-cm radius, 60° magnetic sectors in a horizontal plane. Positive and negative ions are obtained simultaneously from a single electron beam. The positive ions are extracted, accelerated, mass analyzed, and detected in one direction and the negative ions in the opposite direction. The ion source is at ground potential, and the analyzer tubes and collectors are at ±2000 V. The ionizing electron current of 8 μA is confined by a magnetic field of 110 G. The nominal mass range is 1–350 and a 10% valley is achieved at mass 350. Ions are detected by a magnetic

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