The Electronic Structure of (Diiminopyridine)cobalt(I) Complexes

Quinten Knijnenburg,[a] Dennis Hetterscheid,[a] T. Martijn Kooistra,[a] and
Peter H. M. Budzelaar*[a]

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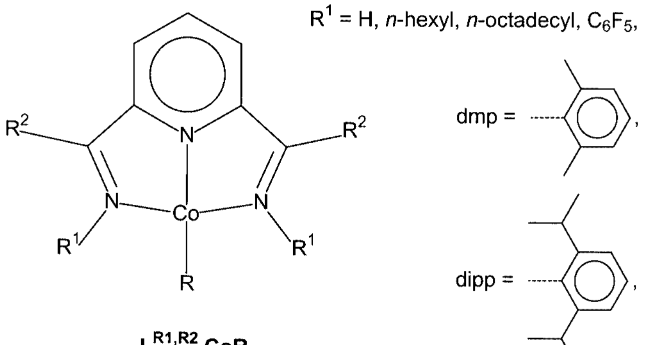
DFT calculations show that square-planar $LCo^{I}R$ complexes of a diiminopyridine ligand are best regarded as containing low-spin Co^{II} antiferromagnetically coupled to a ligand radical anion. The lowest triplet state, corresponding to a $3d_{z^2}\rightarrow\pi^*$ excitation, is calculated to be only a few kcal/mol above the ground state, and is thermally accessible. The anomalous ^1H NMR chemical shifts of the LCoR complexes are suggested to be due to thermal population of the triplet state at room temperature.

Introduction

Diamagnetic square-planar d^8 complexes of Co^I are much rarer[1,2] than the corresponding Rh^I and Ir^I species. Apparently, such Co^I species easily "escape" to the high-spin state or to higher oxidation states like Co^{II} or Co^{III}. Nevertheless, this type of Co^I complex is of great interest because the resemblance to its heavier Rh^I congener might be accompanied by a rich catalytic chemistry similar to that of Rh. Therefore, the recent observation that the diiminopyridine ligand L is able to stabilize Co^I in a low-spin, square-planar state,[3] while still leaving a coordination site available for further chemistry, is significant.



$L^{R1,R2}$ CoR

The complexes $LCo^{I}X$ (X = halide, alkyl) were reported to have unusual ^1H NMR chemical shifts for the pyridine Hγ and imine methyl groups,[3] when compared to the analogous Rh^I and Ir^I species.[4,5] The possibility that these unusual shifts might reflect an unusual electronic structure of the Co^I complexes prompted us to prepare a few additional Co and Rh complexes and to undertake a theoretical investigation of these species. In the present work, we report that the bonding in the Co^I species indeed shows several unexpected features. Diiminopyridine complexes of Co^{II} have been studied theoretically in the context of olefin polymerisation.[6] Experimental[7] and theoretical[8] studies of bis(diiminopyridine) complexes of the first-row transition metals Mn−Zn have revealed the non-innocent character of the ligand and the importance of biradical character in the metal-ligand interaction. The present work shows that biradical character can be even more pronounced in mono(ligand) complexes of cobalt.

Results and Discussion

Synthesis and Characterisation

2,6-Diacetylpyridine, anilines and amines are commercially available. 2,6-Dibenzoylpyridine is easily synthesised by Friedel−Crafts acylation of pyridine-2,6-dicarboxylic acid dichloride and benzene.[9] The diiminopyridine ligands were prepared from the condensation of two equivalents of the appropriate aniline or amine with diacylpyridine. The cobalt dichloride complexes can be synthesised in air. The reduction and subsequent alkylation of the cobalt dichloride complexes to monoalkyl complexes (e.g. $LCoCH_2SiMe_3$) can be achieved in one step using two equivalents of $LiCH_2SiMe_3$, or in two steps via a cobalt monochloride complex, as described earlier.[3] Alkyl complexes [$L^{dipp,Me}CoR$] having the bulky dipp group at R^1 react with hydrogen to form the hydride [$L^{dipp,Me}CoH$]. This complex is very reactive and could not be isolated in pure form, so it was only characterised by NMR spectroscopy. The complexes [LCoR], bearing smaller substituents at R^1 (dmp, alkyl), also react with hydrogen, but after reaction no reson-

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[a] Metal-Organic Chemistry, University of Nijmegen,
Toernooiveld 1, 6525 ED Nijmegen, The Netherlands
Fax: (internat.) +31-24-355-3450
E-mail: budz@sci.kun.nl

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ances due to Co complexes could be recognized in the spectra. The chloride complexes [LCoCl] do not react with hydrogen. The rhodium complex [$L^{dipp,Me}$RhCl] can be easily converted into the desired alkyl complex by addition of alkyllithium. This demonstrates the importance of steric shielding of the metal: the analogous but more open complex [$L^{dmp,Me}$RhCl] could only be converted into the alkyl by an elaborate indirect route.[4]

Structures and Lowest-Energy States of [LCoR] Complexes

The Rh and Ir model complexes [$L^{H,Me}$MR] (M = Rh, Ir; R = H, Me, Cl) have normal closed-shell ground states stable to symmetry breaking. In contrast, for all cobalt complexes studied theoretically the restricted DFT (b3lyp) solution is unstable. The unrestricted $m_S = 0$ solution ("U_0") is 10−20 kcal/mol lower in energy, depending on the ligand. At the restricted DFT (RDFT) level, the optimised structures of the hydride and methyl complexes are non-planar, with the hydride or methyl group bent out of the coordination plane by a significant amount (typically around 20°). Re-optimisation at the unrestricted DFT (UDFT) level, however, results in planar or near-planar structures in all cases.[10]

In the optimised geometries, the Co−N (Table 1) and Co−Cl distances are systematically too large by about 0.04

Table 1. Calculated bond lengths (Å) and singlet-triplet separations (kcal/mol) for $L^{R1,R2}$MR complexes

M	R	R^1	R^2	State[a]	$M-N_{py}$	$M-N_{im}$	$C-N_{im}$	$C_{py}-C_{im}$	ΔE_{ST} [b]
Co	H	H	Me	s	1.881	1.894	1.328	1.452	7.3 (5.5)
				t	1.891	1.922	1.326	1.454	
	Me			s	1.884	1.898	1.328	1.452	8.5 (7.6)
				t	1.897	1.928	1.327	1.452	
	Cl			s	1.840	1.901	1.318	1.454	9.1 (8.7)
				t	1.857	1.923	1.321	1.452	
Rh	H	H	Me	s	2.001	2.035	1.313	1.470	9.9
				t	2.042	2.070	1.328	1.456	
	Me			s	1.990	2.040	1.314	1.467	12.6
				t	2.038	2.073	1.329	1.456	
	Cl			s	1.927	2.032	1.310	1.464	18.7
				t	1.973	2.060	1.324	1.452	
Ir	H	H	Me	s	2.005	2.027	1.322	1.462	17.2
				t	2.054	2.063	1.336	1.453	
	Me			s	1.990	2.029	1.324	1.459	21.0
				t	2.049	2.058	1.336	1.455	
	Cl			s	1.925	2.029	1.320	1.456	26.4
				t	1.979	2.059	1.332	1.449	
Co	H	*n*-C_6H_{13}	Me	s	1.867	1.931	1.328	1.455	5.7
				t	1.876	1.948	1.330	1.454	
	Me			s	1.878	1.960	1.328	1.452	6.3
				t	1.890	1.983	1.330	1.451	
	Cl			s	1.834	1.955	1.321	1.453	8.0
				t	1.850	1.967	1.326	1.451	
	H	dipp	Me	s	1.871	1.944	1.332	1.452	5.6
				t	1.882	1.966	1.333	1.451	
	Me			s	1.881	1.965	1.332	1.450	7.2
				t	1.892	1.990	1.333	1.449	
	Cl			s	1.836	1.972	1.323	1.451	8.4
				t	1.852	1.984	1.329	1.448	
	H	C_6F_5	Me	s	1.882	1.930	1.338	1.451	5.1
				t	1.884	1.951	1.338	1.450	
	Me			s	1.892	1.949	1.339	1.448	6.4
				t	1.896	1.977	1.338	1.447	
	H	dmp	Ph	s	1.876	1.930	1.339	1.459	4.6
				t	1.882	1.952	1.338	1.460	
	Me			s	1.890	1.961	1.338	1.456	6.1
				t	1.894	1.989	1.337	1.456	
	H	dmp	CF_3	s	1.882	1.914	1.337	1.455	6.4
				t	1.890	1.946	1.332	1.456	
	Me			s	1.898	1.945	1.336	1.451	8.3
				t	1.902	1.982	1.331	1.452	
Co	H	H	Me	s	1.870	1.907	1.324	1.454	6.9
(pyrazine!)				t	1.876	1.935	1.324	1.453	
	H	H	(Me_2P)	s	1.947	1.953	1.607	1.803	5.1
(phosphinimine!)				t	1.967	1.963	1.611	1.801	

[a] s = U_0 state for Co, RDFT singlet for Rh, Ir; t = $U_1(z^2)$ triplet. [b] In kcal/mol, estimated from U_0 and $U_1(xz)$ energies (see text); b3lyp/SV(P); for M = Co, R^1 = H, R^2 = Me: values calculated using the TZVPP basis set at the b3lyp/SV(P) geometries given in parentheses.

Å, as is evident from a comparison with the X-ray structures shown in Figure 1. The calculated Co−C distance appears to be about right, but this agreement is fortuitous, since the experimental value is for a CH_2SiMe_3 group while the calculated value is for a Me group, which *should* have a shorter Co−C distance.[11] Thus, Co simply appears to be too large in the calculations. Distances *within* the ligand are reproduced satisfactorily.

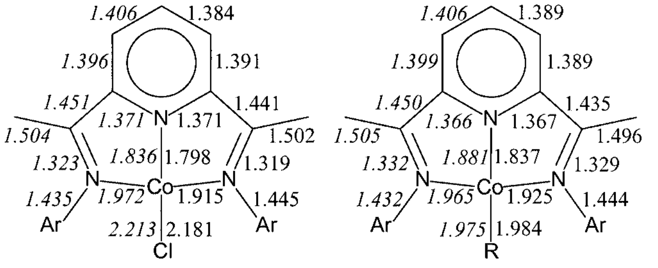
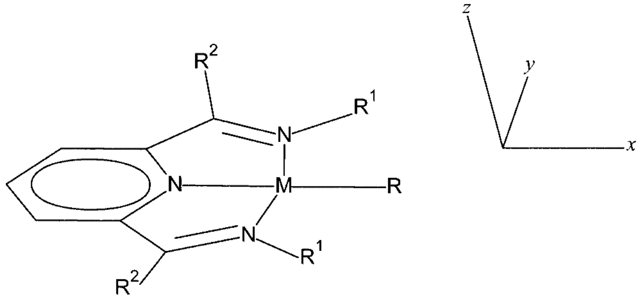


Figure 1. Observed and *calculated* bond lengths for $[L^{dipp,Me}CoR]$ complexes: R = Cl[3a] (left) and CH_2SiMe_3 [3b] or *Me* (right)



The U_0 wavefunctions have S^2 values of 0.80−1.05.[12a] They have one "pair" of occupied α and β orbitals, corresponding to bonding and antibonding combinations of the metal $3d_{xz}$ and ligand π* orbitals, respectively (Figure 2). The remaining orbitals are all fairly cleanly paired. This means that the U_0 "states" are nearly 50:50 mixtures of singlet and triplet states, where the relevant triplet state corresponds to the $3d_{xz}$→π* excitation of a hypothetical true $[LCo^IR]$ species. These triplets, indicated here by $U_1(xz)$, were also obtained separately from unrestricted $m_S = 1$ calculations, and they have S^2 values of 2.00−2.10, indicating little spin contamination. The true singlet energies were then estimated from the energies ε_0, ε_1 of the unrestricted solutions U_0, $U_1(xz)$ and their S^2 values by extrapolating the presumed linear relation between energy and S^2 to $S^2 = 0$ [Equation (1)]:[12b,13]

$$\varepsilon_S \approx \frac{S_1^2\varepsilon_0 - S_0^2\varepsilon_1}{S_1^2 - S_0^2} \qquad (1)$$

The singlet-triplet separation calculated from this varies between 9 and 13 kcal/mol. These results show that the singlet ground state is best described as a square-planar, low-spin $Co^{II}R$ fragment ($3d_{xz}$ singly occupied) antiferromagnetically coupled to a ligand radical anion. In this respect, these complexes are more extreme than the L_2Co^+ complexes considered in earlier work,[8] where only about half of the 3d→π* transfer of electron density was in the form of unpaired electron density, the remainder being "classical" back-donation. Related to this, complexes [LMnR] have been shown to contain a ligand radical anion antiferromagnetically coupled to a *high-spin* Mn^{II} centre.[14] If the ligand is simply considered as a uni-negative ligand and its unpaired electron is ignored, complexes [LCoR] can be seen as relatives of the (also square-planar) low-spin Co^{II} amido complex $[CoBz\{N(SiMe_2CH_2PPh_2)_2\}]$.[15] Thus, reduction of high-spin $[LCoCl_2]$ to low-spin [LCoCl][3] actually occurs at the ligand rather than at the metal, but is accompanied by a spin flip at the metal, possibly induced by the higher ligand-field of the ligand radical anion. A related reduction-induced spin flip was observed in L_2Mn^{2+}.[7]

Interestingly, the $U_1(xz)$ triplet is not the lowest-lying triplet state. According to our calculations, the $U_1(z^2)$ ($3d_{z^2}$→π*) triplet is the lowest one; this always lies about 3−5 kcal/mol below the $U_1(xz)$ triplet and hence about 4.5−9 kcal/mol above the singlet ground state. The geometries calculated for U_0 and $U_1(z^2)$ are very similar, typically differing by less than 0.01 Å in bond lengths. The clearest exception is the $Co-N_{im}$ bond, which can be up to 0.03 Å longer in the triplet state.

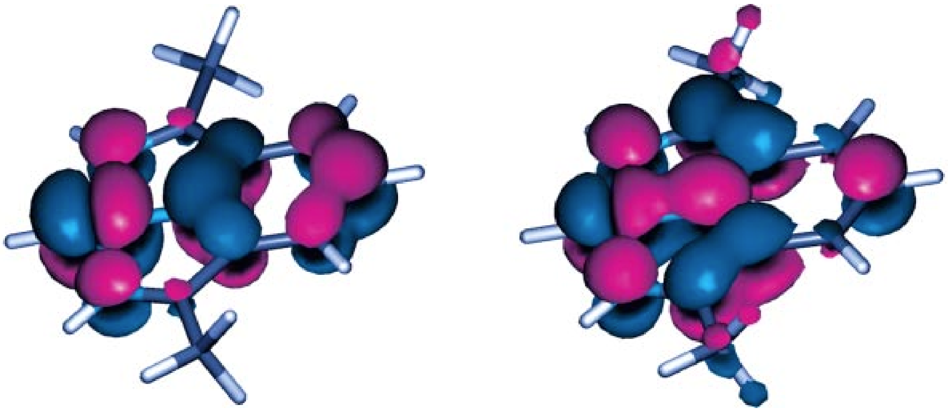


Figure 2. Singly occupied UDFT α- and β-orbitals of U_0 solution for $[L^{H,Me}CoH]$

Substituent Effects on the Singlet-Triplet Separation in Co Complexes

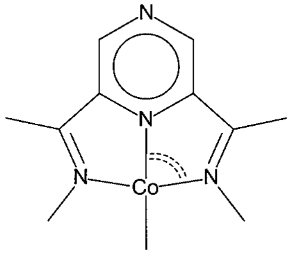
In order to check whether the unusual bonding described above applies not only to simple models but also to "real" systems, we have studied a number of combinations of substituents. Table 1 shows the calculated geometries and singlet-triplet gaps for all systems studied. All values have been calculated at the b3lyp/SV(P) level. For the smallest model system $L^{H,Me}$, we have also calculated energies with the TZVPP basis set. This resulted in somewhat smaller gaps, especially for the hydride. It is likely that basis-set improvement would also lower the gaps for the other systems. However, such calculations are not feasible for the large systems studied here.

The most remarkable result is probably that the singlet-triplet gaps are so insensitive to changes in R, R^1 and R^2. Interpreting the small changes we do see is not so easy, given that they correspond to an excitation from a $3d_{xz}\rightarrow\pi^*$ *singlet* to a $3d_{z^2}\rightarrow\pi^*$ *triplet*. Since, however, we find that the energy difference between the $3d_{xz}\rightarrow\pi^*$ and $3d_{z^2}\rightarrow\pi^*$ triplets is fairly constant, we need only discuss the $3d_{xz}\rightarrow\pi^*$ singlet to $3d_{xz}\rightarrow\pi^*$ triplet gap. This gap, which in the wavefunction picture corresponds to an exchange integral, will be larger if the regions of high electron density of the relevant metal and ligand orbitals (mainly Co $3d_{xz}$ and N $2p_z$) overlap more. Changes in any of the groups R, R^1 and R^2 are therefore expected to affect the gap in two different ways. Steric hindrance at nitrogen will weaken the Co−imine coordination and hence decrease the gap. However, electronic factors that strengthen the pyridine and/or imine coordination will increase the gap.

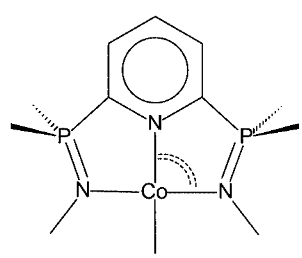
We consistently see an increasing gap when changing R in the order H < Me < Cl, in steps of about 1 kcal/mol. This is presumably a direct electronic effect: in this order, the *trans* effect of the R group decreases and the $Co-N_{py}$ distance decreases (by 0.03−0.04 Å).

Introducing bulky groups at nitrogen (R^1 = *n*-hexyl or dipp, compared to R^1 = H) decreases the gap by about 2 kcal/mol. This is probably a mostly steric effect: the $Co-N_{im}$ distance is 0.04−0.05 Å longer for these *N*-substituted derivatives. Introducing instead the very electron-withdrawing C_6F_5 group at N has very little additional effect, decreasing the gap further by only 0.5 kcal/mol. Since the steric effects of C_6F_5 and dipp should be similar here, it is clear that the electronic effect is rather small. Replacing the backbone (R^2) methyl groups by phenyls has a somewhat larger effect (about 1 kcal/mol for $L^{dmp,Ph}$ relative to $L^{dipp,Me}$). This is most likely due to increased delocalisation of the ligand π*-orbital. The effect is modest because the phenyls cannot become coplanar with the ligand skeleton for steric reasons. Surprisingly, replacing the backbone methyls by CF_3 groups results in an *increase* of the gap by about 1 kcal/mol. At the same time, the Co−imine distance decreases by about 0.03 Å, indicating that the CF_3 substituents strengthen the Co−imine coordination,[16] which is consistent with the increased gap.

Finally, we have considered two more exotic systems: diiminopyrazine and bis(phosphinimino)pyridine. Complexes of the diiminopyrazine ligand show a singlet-triplet gap that is marginally smaller than that calculated for the diiminopyridine complexes. The Co-ring nitrogen distance is slightly smaller, and the Co−imine distances are slightly larger, due to the replacement of Cγ by the smaller nitrogen atom. It is remarkable that such a major change in the π-acceptor character of the ligand has so little effect on the gap. Perhaps the reason is that the diiminopyridine and diiminopyrazine complexes are all completely biradicals, so the variation in ligand π-acceptor strength does not influence the electronic structure.



diiminepyrazine



bis(phosphinimine)pyridine

The bis(phosphinimine)pyridine system,[17] too, is fully a biradical. For this ligand, we calculate a gap which is smaller by about 2 kcal/mol, i.e. as much as is attainable using substituent effects *within* the diiminopyridine system. The most likely explanation is that here the N−Co−N angles are closer to their ideal value of 90°. The exchange integral determining the gap is reduced because the N $2p_z$ orbitals are now closer to a nodal plane of the $3d_{xz}$ orbital. It looks like bis(phosphinimino)pyridines can be considered as a useful extension (in an electronic sense) of the diiminopyridine ligands.

Correlation with NMR Results

Table 2 contains the observed ^1H NMR chemical shifts for a number of LMR complexes, some of which were only generated in situ. We concentrate on the data for $L^{dipp,Me}$, although the other ligands behave similarly. NMR spectroscopic data for several Co^I complexes have already been reported.[3] The shifts for pyridine Hβ are fairly normal. However, for Co the Hγ resonance shows an abnormal low-field shift with increasing ligand field of the group R, from δ = 9.53 ppm for [$L^{dipp,Me}$CoCl] to δ = 10.80 ppm for [$L^{dipp,Me}$CoH]. Even the value for [$L^{dipp,Me}$CoCl] is already high, given that this resonance is found at δ = 7.97 ppm for the free ligand and at δ = 7.80 ppm for [$L^{dipp,Me}$RhCl]. Simultaneous with the low-field shift of the Hγ resonance, the imine methyl (R^2) group shifts from δ = 2.30 ppm (for free $L^{dipp,Me}$) via δ = 0.05 ppm (for [$L^{dipp,Me}$CoCl]) to δ = −1.65 ppm (for [$L^{dipp,Me}$CoH]), while for Rh it never goes below δ = +0.7 ppm. The magnitudes of these curious shifts are emphasised in Table 3, where for Hβ, Hγ and imine Me the values for Co are given relative to the corresponding Rh values.

Table 2. NMR spectroscopic data for diiminopyridine complexes of Co^{I} and Rh^{I}[a]

Ligand R^1,R^2	Complex	Pyridine		Imine	N-alkyl			
		Hβ	Hγ	CH_3	$C^{\alpha}H_2$	$C^{\beta}H_2$	$C^{\gamma}H_2$	$C^{\delta}H_2$
dipp,Me	free L	8.59	7.97	2.30				
	LCoCl	6.91	9.53	0.05				
	$LCoCH_2SiMe_3$	7.62	9.89	−0.85				
	LCoBz	7.68	10.27	−1.16				
	LCoMe	7.86	10.19	−1.15				
	LCoEt	7.99	10.25	−1.33				
	LCoH	7.60	10.80	−1.65				
	LRhCl	6.85	7.80	1.07				
	$LRhCH_2SiMe_3$	7.21	8.06	0.87				
	LRhMe	7.24	8.10	0.72				
	LRhBz	7.06	7.84	0.79				
dmp,Me	$LCoCH_2SiMe_3$	7.71	10.06	−1.28				
dmp,Ph	$LCoCH_2SiMe_3$		9.91	n/a				
n-C_6H_{13},Me	$LCoCH_2SiMe_3$	7.31	9.71	−0.16	5.19	2.22	1.55	1.23
n-$C_{18}H_{37}$,Me	$LCoCH_2SiMe_3$	7.31	9.71	−0.15	5.21	2.26	1.59	

[a] δ (ppm), in C_6D_6, 20 °C.

Table 3. Estimated "anomalous" shifts ($\Delta\delta = \delta_{LCoX} - \delta_{LRhX}$) of $L^{dipp,Me}$ complexes

Complex	Pyridine		Imine
	Hβ	Hγ	CH_3
LCoCl	−0.06	+1.73	−1.02
$LCoCH_2SiMe_3$	+0.41	+1.83	−1.72
LCoBz	+0.62	+2.35	−2.12
LCoMe	+0.62	+2.09	−1.87
LCoH[a]	+0.36	+2.70	−2.37

[a] Using LRhMe as reference.

It is tempting to correlate these NMR shifts with the remarkable electronic structures of the LCoR complexes. The biradical character of singlet LCoR should not, by itself, result in anomalous NMR shifts. However, the calculated singlet-triplet gaps for the "real" systems are rather small (5−8 kcal/mol) and are expected to become smaller with larger basis sets: a decrease of 1.8 kcal/mol is calculated for the model system [$L^{H,Me}$CoH] on going from SV(P) to TZVPP (Table 1). Thus, the extrapolated gap for [$L^{dipp,Me}$CoH] at the b3lyp/TZVPP level is only 3.8 kcal/mol. Allowing for an error of only a few kcal/mol in the gaps we could already have a sizeable thermal population of the triplet state. Rapid spin-flip would then result in averaged shifts containing a contribution of the triplet-state paramagnetic shift. With an estimated Fermi contact term a of −1.5 G for Hγ[18] and an anomalous NMR shift of about 2 ppm, the fraction, f, of triplet population of [$L^{dipp,Me}$CoMe] calculated from Equation (2) should be about 2%, corresponding to a singlet-triplet gap of about 2 kcal/mol.

$$\Delta\delta \approx f\,\frac{\boldsymbol{a}\,\gamma_e^2\,\eta}{4\gamma_H\,kT} \qquad (2)$$

At present, we have no way of verifying this hypothesis. At room temperature, no triplet EPR signal is observed, but this would not be expected anyway because of rapid relaxation. At 4 K, where a signal should normally be observable, the triplet population would be so small as to escape detection. Temperature-dependent ^{1}H NMR studies are hampered by solubility and (especially for the more interesting alkyls) stability problems.

The anomalous shifts increase with decreasing singlet-triplet gap, which agrees with the above hypothesis. However, the changes in observed shifts suggest that the triplet population changes only by a factor of about two over the whole range of Cl···H, corresponding to a gap change of about 0.3 kcal/mol, smaller than our calculated change of about 2 kcal/mol.

Conclusions

[$LCo^{I}X$] complexes have a diamagnetic ground state with a square-planar coordination geometry. In contrast to their heavier Rh^{I} and Ir^{I} analogues, they are best regarded as containing low-spin Co^{II} antiferromagnetically coupled to a ligand radical anion. The lowest-lying triplet state, corresponding to a $3d_{z^2}\rightarrow\pi^*$ excitation, lies only a few kcal/mol above the ground state. The singlet-triplet separation decreases with increasing ligand-field strength of the group X at Co. We suggest that the anomalous ^{1}H NMR shifts observed for these Co complexes, but not for their Rh and Ir analogues, are due to thermal population of the triplet state at room temperature. The triplet state is so low in energy that it can certainly be involved in chemical reactions. Obviously, the availability of both a singlet biradical and a triplet state multiplies the number of reaction paths accessible to the complex. Whether this is relevant to polymerisation catalysis of LCo complexes remains to be established.

Experimental Section

General Remarks: All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques or in a conventional nitrogen-filled glove box. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. NMR spectra were recorded on Varian and Bruker spectrometers at ambient temperature. Commercially available chemicals were used as received. The starting material 2,6-dibenzoylpyridine,[9] the ligands $\mathrm{L^{dmp,Me}}$ and $\mathrm{L^{dipp,Me}}$ [19] and the complexes $[\mathrm{L^{dipp,Me}Rh^{I}Cl}]$,[20] $[\mathrm{L^{dipp,Me}Co^{II}Cl_2}]$, $[\mathrm{L^{dmp,Me}Co^{II}Cl_2}]$,[19] $[\mathrm{L^{dipp,Me}Co^{I}Cl}]$, $[\mathrm{L^{dipp,Me}Co^{I}CH_3}]$, $[\mathrm{L^{dipp,Me}Co^{I}Bz}]$ and $[\mathrm{L^{dipp,Me}Co^{I}CH_2SiMe_3}]$[3] were synthesised according to literature procedures.

Methods: All calculations were carried out with the Turbomole program[21] coupled to the PQS Baker optimiser.[22] Geometries were fully optimised at the unrestricted ("singlet" or "triplet") b3-lyp level[23] using the Turbomole SV(P) basis set on all atoms (pseudopotential basis on Co). For the smallest model system, improved final energies were then obtained from single-point calculations using a TZVPP basis and a fine ("m4") integration grid. Zero-point energy (ZPE) and thermal corrections were not included. Orbital plots were prepared using Molden.[24] For triplet states of a minimal model system ($R^1 = R^2 = H$, R = Cl, Me, H) Fermi contact terms were estimated using the Gaussian 98 package,[25] a LANL2DZ basis[26] for the metal atom, and the 6-31G* basis[27] for the ligand atoms.

$\mathrm{L^{dmp,Ph}}$: 2,6-Dibenzoylpyridine (1.50 g, 5.23 mmol) and dimethylaniline (0.60 g, 4.96 mmol; 0.95 equiv.) were dissolved in benzene (50 mL). After the addition of a small amount of camphorsulfonic acid, the solution was refluxed overnight, using a Dean−Stark water trap. The solution was placed in the dark for a week over molecular sieves. Recrystallisation from hot methanol offered 0.30 g of yellow needles, which, according to GC analysis, consisted of 82% of the desired product together with 18% of the monocondensed product.

$\mathrm{L^{hex,Me}}$: 2,6-Diacetylpyridine (1.00 g, 6.13 mmol) and *n*-hexylamine (1.245 g, 12.27 mmol, 2.0 equiv.) were dissolved in benzene (50 mL). After the addition of a small amount of camphorsulfonic acid, the solution was refluxed overnight, using a Dean−Stark water trap. The solvent was removed in vacuo, and 1.83 g (90.9%) of product was obtained as a yellow oil. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ = 7.96 (d, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 2 H, Py *H*β), 7.59 (t, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 1 H, Py *H*γ), 3.42 (t, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 4 H, hex *H*α), 2.29 (s, 6 H, N=C*Me*), 1.64 (quint, 4 H, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, hex *H*β), 1.26 (m, 12 H, hex *H*γδε), 0.80 (t, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 6 H, hex *H*ζ) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ = 166.33 (N=*C*), 156.26 (Py *C*α), 136.45 (Py *C*γ), 120.85 (Py *C*β), 52.57 (hex *C*α), 31.77, 30.81, 27.39, 22.65 (hex *C*β−ε), 14.05 (hex *C*ζ), 13.61 (N=C*Me*) ppm.

$\mathrm{L^{octadec,Me}}$: 2,6-Diacetylpyridine (1.00 g, 6.13 mmol) and *n*-octadecylamine (3.30 g, 12.26 mmol, 2 equiv.) were dissolved in benzene (50 mL). After the addition of a small amount of acetic acid, the solution was refluxed overnight, using a Dean−Stark water trap. The solvent was removed in vacuo yielding a yellow oil, which solidified upon cooling with ice. The yield was 3.88 g (95%). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ = 7.98 (d, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 2 H, Py *H*β), 7.59 (t, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 1 H, Py *H*γ), 3.43 (t, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 4 H, octadec *H*α), 2.28 (s, 6 H, N=C*Me*), 1.66 (quint, 4 H, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, octadec *H*β), 1.25−0.90 (m, 60 H, octadec *H*γ-ρ), 0.80 (t, $^{3}J_{\mathrm{H,H}}$ = 6.8 Hz, 6 H, octadec *H*ς) ppm. ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): δ = 167.0 (N=*C*), 156.9 (Py *C*α), 137.1 (Py *C*γ), 121.6 (Py *C*β), 53.3 (octadec *C*α), 32.6, 31.5, 30.4 (several), 30.1, 28.4, 23.3, 14.8 (octadec *C*β−ς), 14.3 (N=C*Me*) ppm.

$[\mathrm{L^{dmp,Ph}Co^{II}Cl_2}]$: Part of the mixture of mono- and dicondensed dibenzoylpyridine (0.30 g containing 499 μmol of $\mathrm{L^{dmp,Ph}}$) and $\mathrm{CoCl_2{\cdot}6H_2O}$ (0.15 g, 630 mmol, 1.26 equiv.) were dissolved in 10 mL of THF. Almost immediately a colour change could be observed and a golden brown solid precipitated. After stirring for an additional hour at room temperature, this solid was filtered off, washed twice with THF (5 mL) and dried in vacuo. The yield was 0.195 g (63.8%). ^{1}H NMR (200 MHz, $\mathrm{CD_2Cl_2}$): δ = 108.80 (2 H, Py *H*β), 37.45 (1 H, Py *H*γ), 6.04, 5.74, −1.37 (3 × 4 H, Ph $H_{\mathrm{o,m}}$, dmp H_{m}), 3.20 (2 H, Ph H_{p}), −11.62 (2 H, dmp H_{p}), −26.99 (12 H, dmp *Me*) ppm.

$[\mathrm{L^{hex,Me}Co^{II}Cl_2}]$: $\mathrm{L^{hex,Me}}$ (2.16 g, 6.55 mmol) and $\mathrm{CoCl_2{\cdot}6H_2O}$ (1.16 g, 4.87 mmol; 0.74 equiv.) were dissolved in 50 mL of THF and stirred for 15 min. The solvent was removed in vacuo, leaving 2.83 g (102%, presumably containing some residual THF) of the red-brown product. ^{1}H NMR (400 MHz, $\mathrm{CD_2Cl_2}$): δ = 104.14 (2 H, Py *H*β), 71.35 (4 H, hex *H*α), 13.90 (1 H, Py *H*γ), −1.55 (6 H, hex *H*ζ), −3.25 (4 H, hex *H*ε), −5.12 (6 H, N=C*Me*), −7.12 (4 H, hex *H*δ), −12.88 (4 H, hex *H*γ), −39.74 (4 H, hex *H*β) ppm.

$[\mathrm{L^{octadec,Me}Co^{II}Cl_2}]$: $\mathrm{L^{octadec,Me}}$ (1.10 g, 1.65 mmol) and $\mathrm{CoCl_2{\cdot}6H_2O}$ (0.39 g, 1.64 mmol, 1.0 equiv.) were dissolved in 20 mL of THF and stirred for an hour. The solvent was removed in vacuo, leaving 1.21 g (93%) of the red-brown product. ^{1}H NMR (200 MHz, $\mathrm{CD_2Cl_2}$): δ = 106.0 (2 H, Py *H*β), 71.7 (4 H, octadec *H*α), 14.1 (1 H, Py *H*γ), −5.6 (6 H, N=C*Me*), 1.7, 1.4−0.8 (several), 0.5, 0.2, −1.6, −3.6, −7.1, −13.4, −41.1 (68 H, octadec, *H*β-ς) ppm.

$[\mathrm{L^{dipp,Me}Co^{I}H}]$: This complex was generated in situ by addition of 2 mL of $\mathrm{H_2}$ to an NMR sample of $[\mathrm{L^{dipp,Me}Co^{I}CH_2SiMe_3}]$. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ = 10.80 (t, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 1 H, Py *H*γ), 7.60 (m, 4 H, Py *H*β, dipp H_{p}), 7.46 (d, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 4 H, dipp H_{m}), 3.41 (sept, 4 H, $^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, C*H*Me₂), 1.31 and 0.29 (d, 12H each, $^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, CH*Me*₂), −1.65 (s, 6 H, N=C*Me*) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 168.5 (N=*C*), 160.1 (dipp C_{i}), 156.5 (Py *C*α), 140.2 (dipp C_{o}), 126.3 (dipp C_{p}), 124.1 (dipp C_{m}), 123.6 (Py *C*β), 117.8 (Py *C*γ), 28.6 (*C*HMe₂), 25.4 (N=C*Me*), 23.3 and 22.5 (CH*Me*₂) ppm.

$[\mathrm{L^{dipp,Me}Co^{I}Et}]$: This complex was generated in situ by addition of 2 mL of ethene to an NMR sample of $[\mathrm{L^{dipp,Me}Co^{I}H}]$. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ = 10.25 (t, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 1 H, Py *H*γ), 7.99 (d, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 2 H, Py *H*β), 7.52 (t, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 2 H, dipp H_{p}), 7.39 (d, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 4 H, dipp H_{m}), 3.13 (sept, 4 H, $^{3}J_{\mathrm{H,H}}$ = 6.7 Hz, C*H*Me₂), 1.51 (q, 2 H, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, CoC*H*₂CH₃), 1.17 and 0.75 (d, 12H each, $^{3}J_{\mathrm{H,H}}$ = 6.7 Hz, CH*Me*₂), −1.19 (t, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 3 H, CoCh₂C*H*₃) −1.33 (s, 6 H, N=C*Me*) ppm. ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$): δ = 165.3 (N=*C*), 157.9 (dipp C_{i}), 154.9 (Py *C*α), 140.9 (dipp C_{o}), 126.6 (dipp C_{p}), 124.1 (dipp C_{m}), 122.6 (Py *C*β), 117.6 (Py *C*γ), 28.3 (*C*HMe₂), 26.1 (N=C*Me*), 24.2 and 23.1 (CH*Me*₂) 12.8 CoCH₂*C*H₃ ppm. The signal for Co*C*H₂ was not observed.

$[\mathrm{L^{dmp,Me}Co^{I}CH_2SiMe_3}]$: $[\mathrm{L^{dmp,Me}Co^{II}Cl_2}]$ (0.276 g, 553 μmol) was added to a solution of $\mathrm{LiCH_2SiMe_3}$ (0.115 g, 1.21 mmol; 2 equiv.) in 8 mL of hexane. The mixture was stirred for one hour, after which it was filtered. The filtrate was evaporated to dryness; the yield was not determined. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ = 10.06 (t, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 1 H, Py *H*γ), 7.71 (d, $^{3}J_{\mathrm{H,H}}$ = 7.8 Hz, 2 H, Py *H*β), 7.34 (d, $^{3}J_{\mathrm{H,H}}$ = 6.2 Hz, 2 H, dmp H_{p}), 7.26 (d, $^{3}J_{\mathrm{H,H}}$ = 6.2 Hz, 4 H, dmp H_{m}), 0.80 (s, 2 H, CoC*H₂*), −0.63 (s, 9 H, Si*Me₃*), −1.28 (s, 6H N=C*Me*) ppm. The addition of $\mathrm{H_2}$ to the NMR sample resulted in a colour change from deep red-purple to green and disappearance of all the complex-related ^{1}H NMR signals.

$[\mathrm{L^{dmp,Ph}Co^{I}CH_2SiMe_3}]$: $[\mathrm{L^{dmp,Ph}Co^{II}Cl_2}]$ (0.195 g, 313 μmol) was added to a solution of $\mathrm{LiCH_2SiMe_3}$ (0.065 g, 684 μmol, 2.2 equiv.)

in 5 mL of hexane. An immediate colour change to green was observed. After 2 h the mixture was filtered, and the filtrate was evaporated to dryness, yielding a green powder (yield not determined). ^{1}H NMR (200 MHz, C_6D_6): δ = 9.91 (t, $^{3}J_{H,H}$ = 8 Hz, 1 H, Py *H*γ) ppm. The rest of the peaks could not be unambiguously assigned. The addition of H_2 to the NMR sample resulted in disappearance of all the complex-related ^{1}H NMR signals.

[$L^{hex,Me}Co^{I}CH_2SiMe_3$]: A 1 M solution of $LiCH_2SiMe_3$ (1.6 mL, 1.60 mmol, 2.0 equiv.) in pentane and 8 mL of hexane were added to [$L^{hex,Me}Co^{II}Cl_2$] (0.45 g, 0.79 mmol). The mixture was stirred for one hour, after which it was filtered. The filtrate was evaporated to dryness, yielding 0.153 g of [$L^{hex,Me}Co^{I}CH_2SiMe_3$] (33.8%) as a thick dark-red oil. ^{1}H NMR (200 MHz, C_6D_6): δ = 9.72 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, Py *H*γ), 7.31 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, Py *H*β), 5.19 (t, $^{3}J_{H,H}$ = 7.6 Hz, 4 H, hex *H*α), 2.22 (quint, $^{3}J_{H,H}$ = 7.6 Hz, 4 H, hex *H*β), 1.54 (quint, $^{3}J_{H,H}$ = 7.6 Hz, 4 H, hex *H*γ), 1.22 (m, 8 H, hex *H*δ, ε), 0.82 (t, $^{3}J_{H,H}$ = 7.2 Hz, 6 H, hex *H*ζ), 0.02 (s, 2 H, CoCH_2), −0.14 (s, 9 H, Si*Me*$_3$), −0.18 (s, 6 H, N=C*Me*) ppm. ^{13}C NMR (75 MHz, C_6D_6): 162.42 (N=*C*), 152.18 (Py *C*α), 122.50 (Py *C*β), 114.01 (Py *C*γ), 59.35 (hex *C*α), 32.20 and 22.89 (hex *C*δ, ε), 29.08 and 27.36 (hex *C*β, γ), 20.39 (N=C*Me*), 14.21 (hex *C*ζ), 3.00 (Si*Me*$_3$) ppm. The signal for CoCH_2 was not found. The addition of H_2 to the ^{1}H NMR sample resulted in a colour change from dark red to green-brown and a loss of all the complex-related ^{1}H NMR signals.

[$L^{octadec,Me}Co^{I}CH_2SiMe_3$]: A 1 M solution of $LiCH_2SiMe_3$ (0.90 mL, 900 µmol, 2.45 equiv.) in pentane and 8 mL of hexane were added to [$L^{octadec,Me}Co^{II}Cl_2$] (0.292 g, 368 µmol). The mixture was stirred for two hours, after which it was filtered, and the solvent was removed in vacuo leaving a deep purple-red product. ^{1}H NMR (400 MHz, C_6D_6): δ = 9.71 (t, $^{3}J_{H,H}$ = 7.6 Hz, 1 H, Py *H*γ), 7.31 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, Py *H*β), 5.21 (t, $^{3}J_{H,H}$ = 7.6 Hz, 4 H, octadec *H*α), 2.26 (quint, $^{3}J_{H,H}$ = 7.6 Hz, 4 H, octadec *H*β), 1.59 (quint, $^{3}J_{H,H}$ = 7.2 Hz, 4 H, octadec *H*γ), 1.5−1.1 (m, 56 H, octadec *H*δ−ρ) ppm. octadec *H*ς is presumably obscured by the resonance of traces of hexane. The signals for CoCH_2, Si*Me*$_3$ and N=C*Me* could not be unambiguously assigned.

[$L^{dipp,Me}Rh^{I}CH_3$]: Toluene (2 mL) was added to a mixture of [$L^{dipp,Me}Rh^{I}Cl$] (100 mg, 0.16 mmol) and MeLi (7.1 mg, 0.32 mmol, 2 equiv.) and the reaction mixture was stirred for three days. The obtained product was filtered off and the filtrate was evaporated to dryness, yielding 91 mg of [$L^{dipp,Me}Rh^{I}CH_3$] (84%) as a dark green solid. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.19 (t, $^{3}J_{H,H}$ = 7.9 Hz, 1 H, Py *H*γ), 7.34 (d, $^{3}J_{H,H}$ = 7.7 Hz, 2 H, Py *H*β), 7.22−7.10 (m, 6 H, dipp $H_{m,p}$), 3.19 (sept., 4 H, $^{3}J_{H,H}$ = 6.8 Hz, *CH*Me$_2$), 2.12 (d, $^{2}J_{RhH}$ = 1.1 Hz, 3 H, Rh*Me*), 0.99 (m, 24 H, CH*Me*$_2$), 0.73 (s, 6 H, N=C*Me*) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 166.8 (N=*C*), 155.3 (d, $^{2}J_{RhC}$ = 2.7 Hz, Py *C*α), 148.3 (dipp C_i), 140.6 (Py *C*γ), 140.4 (dipp C_o), 123.6 (dipp C_m), 123.1 (Py *C*β), 28.2 (*C*HMe$_2$), 23.9 and 23.6 (CH*Me*$_2$), 18.9 (N=C*Me*), 1.2 (d, $^{1}J_{RhC}$ = 21.0 Hz, Rh*Me*) ppm. dipp C_p is presumably obscured by the resonance of the C_6D_6 solvent.

[$L^{dipp,Me}Rh^{I}Bz$]: Toluene (2 mL) was added to a mixture of [$L^{dipp,Me}Rh^{I}Cl$] (100 mg, 0.27 mmol) and Bz_2Mg (41 mg, 0.27 mmol, 1 equiv.). The mixture was stirred for 24 h. The magnesium salts were separated from the reaction products by filtration and the filtrate was evaporated to dryness, yielding a purple powder. Hexane (5 mL) was added, the mixture was filtered and the filtrate was evaporated to dryness, yielding [$L^{dipp,Me}Rh^{I}Bz$] as a purple powder. ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.97 (t, $^{3}J_{H,H}$ = 7.9 Hz, 1 H, Py *H*γ), 7.31−7.17 (m, 8 H, dipp $H_{m,p}$, Py *H*β), 7.21 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2 H, Bz H_m), 6.65 (m, 1 H, Bz H_p), 5.59 (d, $^{3}J_{H,H}$ = 6.9 Hz, 2 H, Bz H_o), 3.69 (d, $^{2}J_{RhH}$ = 2.6 Hz, 2 H, RhCH_2), 3.17 (sept., 4 H, $^{3}J_{H,H}$ = 6.8 Hz, *CH*Me$_2$), 1.01−0.92 (m, 30 H, N=C*Me*, CH*Me*$_2$) ppm. ^{13}C NMR (C_6D_6 75 MHz): δ = 166.8 (d, $^{2}J_{RhC}$ = 2.3 Hz, N=*C*), 156.2 (d, $^{2}J_{RhC}$ = 2.9 Hz, Py *C*α), 151.9 (d, $^{2}J_{RhC}$ = 1.7 Hz, Bz C_i), 148.4 (dipp C_i), 141.0 (Py *C*γ), 140.6 (dipp C_o), 127.3 (Bz C_o), 127.0 (Bz C_m), 126.5 (dipp C_p), 124.2 (dipp C_m), 123.6 (Py *C*β), 119.6 (Bz C_p), 28.6 (*C*HMe$_2$), 24.0 and 23.8 (CH*Me*$_2$), 19.5 (d, $^{3}J_{RhC}$ = 1.7 Hz, N=C*Me*) ppm. The RhCH_2 signal was not detected.

[$L^{dipp,Me}Rh^{I}CH_2SiMe_3$]: A 1.0 M solution of $LiCH_2SiMe_3$ in pentane (0.54 mL 0.54 mmol, 2 equiv.) and 4 mL of toluene were added to [$L^{dipp,Me}Rh^{I}Cl$] (170 mg, 0.27 mmol, 1 equiv.). The mixture was stirred for 24 h. The solvent was removed in vacuo, yielding a green-brown powder. Hexane (5 mL) was added, the mixture was filtered and the filtrate was evaporated to dryness, yielding [$L^{dipp,Me}Rh^{I}CH_2SiMe_3$] as a green powder. ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.06 (t, $^{3}J_{H,H}$ = 7.9 Hz, 1 H, Py *H*γ), 7.24 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2 H, Py *H*β), 7.15−7.03 (m, 6 H, dipp $H_{m,p}$), 3.26 (sept., $^{3}J_{H,H}$ = 6.8 Hz, 4 H, *CH*Me$_2$), 1.87 (d, $^{2}J_{Rh;H}$ = 2.2 Hz, 2 H, RhCH_2), 1.28 and 0.97 (2 × d, $^{3}J_{H,H}$ = 6.6 Hz, 12 H each, CH*Me*$_2$), 0.86 (s, 6 H, N=C*Me*), 0.29 (s, 9 H, Si*Me*$_3$) ppm. ^{13}C NMR (C_6D_6 75 MHz): δ = 165.8 (d, $^{2}J_{RhC}$ = 0.9 Hz, N=*C*), 156.3 (d, $^{2}J_{RhC}$ = 3.2 Hz, Py *C*α), 149.4 (dipp C_i), 141.1 (Py *C*γ), 140.6 (dipp C_o), 126.7 (dipp C_p), 124.3 (dipp C_m), 123.6 (Py *C*β), 28.2 (*C*HMe$_2$), 24.5 and 24.3 (CH*Me*$_2$), 19.9 (d, $^{3}J_{Rh,C}$ = 2.0 Hz, N=C*Me*), 6.7 (d, $^{1}J_{Rh,C}$ = 33.0 Hz, RhCH_2), 4.0 (Si*Me*$_3$) ppm.

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[1] Selected examples of square-planar Co^{I} complexes [all except ref.[1f] with tetradentate and fairly rigid ligands]. Bis(salicylideneiminato): [1a] F. Arena, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1986**, *25*, 4589. [1b] S. Gambarotta, F. Arena, C. Floriani, P. F. Zanazzi, *J. Am. Chem. Soc.* **1982**, *104*, 5082. [1c] G. Fachinetti, C. Floriani, P. F. Zanazzi, A. R. Zanari, *Inorg. Chem.* **1979**, *18*, 3469. Porphyrinato: [1d] P. Doppelt, J. Fischer, R. Weiss, *Inorg. Chem.* **1984**, *23*, 2958. Phthalocyaninato: [1e] H. Huckstadt, H. Homborg, *Z. Anorg. Allg. Chem.* **1998**, *624*, 715. Bis(imino)succinonitrile: [1f] S.-M. Peng, D.-S. Liaw, Y. Wang, A. Simon, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 210. Miscellaneous: [1g] Y.-S. You, G.-H. Lee, S.-M. Peng, *J. Chin. Chem. Soc. (Taipei)* **1996**, *43*, 261.

[2] Co^{I} is more often tetrahedral. Selected examples (without ligand constraints): L_4Co^{+}: [2a] N. Lu, N. C. Norman, A. G. Orpen, M. J. Quayle, P. L. Timms, G. R. Whittell, *J. Chem. Soc., Dalton Trans.* **2000**, 4032. [L_3CoCl]: [2b] R. A. Jones, A. L. Stuart, J. L. Atwood, W. E. Hunter, *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 273. One of the few examples with nitrogen donors is [(tpz)Co(CO)]: [2c] J. L. Detrich, R. Konecny, W. M. Vetter, D. Doren, A. L. Rheingold, K. H. Theopold, *J. Am. Chem. Soc.* **1996**, *118*, 1703.

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[5] E. L. Dias, M. Brookhart, P. S. White, *Organometallics* **2000**, *19*, 4995.

[6] P. Margl, L. Deng, T. Ziegler, *Organometallics* **1999**, *18*, 5701.

[7] B. de Bruin, E. Bill, E. Bothe, T. Weyhermuller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 2936.

[8] P. H. M. Budzelaar, B. de Bruin, A. W. Gal, K. Wieghardt, J. H. Van Lenthe, *Inorg. Chem.* **2001**, *40*, 4649.

[9] N.-E. Andersson, T. O. Soine, *J. Am. Pharm. Ass.* **1950**, *39*, 463.

[10] Burger reported that non-planar structures also form easily for Rh and Ir and are sometimes even preferred.[4] However, in

that case they do not become planar when allowed to go unrestricted, and indeed there is no unrestricted solution lower than the restricted one.

[11] Compare for example, [$(dmg)_2Co(CH_2SiMe_3)(py)$], where Co−C = 2.031 Å: [11a] L. Randaccio, N. Bresciani-Pahor, P. J. Toscano, L. G. Marzilli, *J. Am. Chem. Soc.* **1981**, *103*, 6347; with [$(dmg)_2Co(Me)(im)$], where Co−C = 1.986 Å: [11b] V. Pattabhi, M. Nethaji, E. J. Gabe, F. L. Lee, Y. le Page, *Acta Crystallogr., Sect. C* **1984**, *40*, 1155.

[12] [12a] Usually, unrestricted solutions with $S^2 = 1$ correspond to small singlet-triplet gaps.[13f] However, if the preference of the "pure" singlet for a biradical structure is strong enough, full mixing (leading to $S^2 \approx 1$) will occur also for larger singlet-triplet separations. Apparently, that is the case here. [12b] Noodleman uses Equation (1′), which is similar to Equation (1) but has $\hat{S}_1^2$ set to the ideal value of 2;[13a−13c] Bachler uses a similar expression.[13d,13e]

$$\varepsilon_S \approx \frac{2\varepsilon_0 - S_0{}^2\,\varepsilon_1}{2 - S_0{}^2} \tag{1'}$$

Spin contamination is always present in both the U_0 and U_1 solutions. Contamination of U_0 skews the result of Equation (1′) towards larger gaps. We prefer Equation (1) because it treats spin contamination in U_0 and U_1 on an equal basis. In any case, results obtained with Equation (1′) would differ only marginally from the ones we calculate with Equation (1).

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