

(Py)₂Co(CH₂SiMe₃)₂ As an Easily Accessible Source of "CoR₂"

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(Py)₂CoR₂ (R = CH₂SiMe₃) is easily prepared from (Py)₄CoCl₂ and RLi. It is fairly stable at room temperature and serves as a convenient source of CoR₂ for transfer to other ligands. Unfortunately, (Py)₂CoR₂ was obtained only as an oil, but the structure of the related complex (Py)₂CoR'₂ (R' = CH₂CMe₂Ph) could be confirmed by a single-crystal X-ray diffraction study. Transfer of the CoR₂ fragment from (Py)₂CoR₂ or (TMEDA)CoR₂ to diiminepyridine-type ligands (1–6) was studied as a function of ligand steric and electronic properties. Reaction with *N*-2,6-dimethylphenyl (1) and *N*-2,4,6-trimethylphenyl (2) ligands produced diamagnetic *mono*alkyl complexes; the structure of (1)CoR was confirmed by X-ray diffraction. With the less shielding *N*-phenyl (3) and *N*-benzyl (4) ligands, ¹H NMR indicated formation of diamagnetic Co¹ alkyl species, but they were not stable enough to allow isolation. Fluorinated ligand **5** appears to be less reactive and –despite its supposedly stronger π -acceptor character—also does not lead to formation of a stable Co¹ alkyl complex. With PyBOX ligand **6**, high-spin *di*alkyl complex (6)CoR₂ was observed by ¹H NMR. Based on these observations and DFT calculations, a mechanism is proposed for formation of diiminepyridine Co¹ alkyls that involves formation of a high-spin κ^2 complex, spin flip to give a low-spin κ^3 complex, and irreversible loss of an alkyl radical.

Introduction

Transition metal alkyl complexes are among the more reactive—and therefore more interesting—species in organometallic chemistry. Precisely because of this reactivity, preparing and isolating such species can be a challenge. Conventional wisdom holds that metal alkyls tend to be stable if they (a) are coordinatively saturated (closed-shell 16-*e* or 18-*e*) and (b) have no β -hydrogens. The last decades have seen a surge in interest in the chemistry of paramagnetic first-row transition metal complexes bearing less traditional ligands such as imine, pyridine, and carbene instead of the more common phosphine, cyclopentadienyl, and carbon monoxide. This interest was for a large part fueled by the discovery of Fe and Co Brookhart/Gibson polymerization catalysis using diiminepyridine (DIMPY) ligands.¹



Metal alkyls are likely the active species here, but isolating such alkyls turns out to be nontrivial. For Fe, the standard synthetic route of treating a DIMPY metal dihalide precursor with an alkyllithium reagent works well in selected cases,² but frequently (in particular for less shielding ligands) complications such as reduction, ligand alkylation, and deprotonation occur.^{2,3} An alternative approach is to use a metal dialkyl with labile ligands and displace these by the desired DIMPY ligand. A very convenient FeR₂ "synthon", reported a few years ago by Cámpora,^{4,5} is $(Py)_2FeR_2$ (R = CH₂SiMe₃, CH₂Ph, and CH₂CMe₂Ph), prepared by treating (Py)₄FeCl₂ with RLi or RMgX; its utility was clearly illustrated by the synthesis of [2,6-(2,4,6-Me₃C₆H₂N=CMe)₂- C_5H_3N [Fe(CH₂SiMe₃)₂. The group of Chirik has investigated the scope of this transfer reaction for the synthesis of (DIMPY)Fe dialkyl complexes and found that it is more robust than the FeCl₂/RLi approach, although some side reactions were still observed.2c

For Co, reaction of (DIMPY)CoCl₂ with metal alkyls leads exclusively to reduction, giving either (DIMPY)CoCl

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^{(4) (}a) Cámpora, J.; Marcos Naz, A.; Palma, P.; Álvarez, E. *Organometallics* **2005**, *24*, 4878. (b) (Py)₂Fe(CH₂SiMe₃)₂ was prepared by us according to Cámpora's method and characterized by ¹H NMR.

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Figure 1. ¹H NMR spectra of (A) $(Py)_2CoR_2$ and (B) (TMEDA)CoR₂.

Table 1. Comparison of ¹H NMR Shifts (ppm) for $(Py)_2MR_2$ Complexes (M = Co, Fe)

	$(Py)_2CoR_2$	$(Py)_2FeR_2^4$	(Py) ₂ CoR' ₂	$(Py)_2FeR'_2^4$
Ме	10.3	11.2	21.6	25.2
Py H2	114	129^{a}	108	
Py H3	38.4	35.5	32.7	35.3
Py H4	-8.5	17.4	-8.3	12.9
Ph Ho			10.2^{b}	120
Ph Hm			7.4^{b}	5.4
Ph <i>Hp</i>			3.9	11.8

^{*a*} This work (not reported by Campora⁴). ^{*b*} The assignments of *Ho* and *Hm* could be reversed.

or (DIMPY)CoR, even for hindered DIMPY ligands.⁶ It is not clear at present whether the metal alkyl directly reduces Co or first transfers an alkyl group, which could then be lost as a radical. Unlike for Fe, no convenient CoR₂ equivalent is available that might allow one to circumvent this problem. Hay-Motherwell reported the synthesis and X-ray characterization of (TMEDA)Co(CH₂SiMe₃)₂ nearly 20 years ago, but the complex was obtained in only 11% yield and its isolation is awkward;⁷ as a result, this precursor has not been used frequently. In addition, the group of Theopold has reported the synthesis of ligand-free diaryl complex $[Co(2,4,6-Me_3C_6H_2)_2]_2$, but again synthesis is far from trivial.⁸ The synthesis of the more hindered Co[2,6-(2,4,6-Me₃C₆H₂)₂-C₆H₃]₂ seems to be simpler,⁹ but this complex is so hindered that complexation with ligands like DIMPY is unlikely. Therefore, we decided to check whether Cámpora's approach would also work for Co.

Results and Discussion

Synthesis of $(Py)_2Co(CH_2SiMe_3)_2$. Treatment of " $(Py)_4CoCl_2$ " with RLi (R = CH_2SiMe_3) in pentane at low temperature, followed by slow warming to room temperature, resulted in clean formation of $(Py)_2CoR_2$ as the only

metal complex in solution. After filtration and evaporation of the solvent, the product was obtained as a bright green oil; all attempts at crystallization failed.¹⁰ The ¹H NMR data (see Figure 1A) indicate the overall composition of the complex and are rather similar to those of the Fe analogue (see Table 1) except for the pyridine H4 proton (Co: -8.5ppm; Fe: +17.4 ppm⁴). Use of an internal standard (hexamethylbenzene) allowed determination of the yield (\sim 75%) by NMR. The complex appears to be indefinitely stable under an inert atmosphere at -35 °C and survives for at least several days at room temperature. It is, however, extremely sensitive to air and moisture. A few aspects of the synthesis should be noted:

• The quality of the RLi used is pivotal. We crystallize freshly received RLi from pentane and store it as a solid in a glovebox to maintain its quality.

• (Py)₄CoCl₂ was prepared from anhydrous CoCl₂ rather than from the commonly used hydrated dichloride,¹¹ to avoid potential problems in the reaction with RLi. The complex easily loses part of its coordinated pyridine under vacuum, changing from pink to purple-blue.¹² Ligand loss also occurred when the pink solid was suspended in pentane for the synthesis of (Py)₂CoR₂, but this dissociation did not affect the outcome of the reaction.

• Chirik reported that reacting $(Py)_4FeCl_2$ with only 1 equiv of RLi resulted in formation of $(Py)_2FeRCl.^{2c}$ For Co, we found that use of 1 equiv of RLi produced only $(Py)_2CoR_2$ and unreacted $(Py)_nCoCl_2$.

Since $(Py)_2CoR_2$ could not be obtained in crystalline form, obtaining a satisfactory elemental analysis for this complex was not possible. Therefore, we employed several alternative methods to establish its constitution. First, the purity was estimated at 91% from the ¹H NMR spectrum using an internal standard (hexamethylbenzene). Second, using the same internal standard, the magnetic moment was determined by the Evans NMR method¹³ as 4.8(3) μ_B (average of

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Figure 2. X-ray structure of $(Py)_2CoR'_2$ (thermal ellipsoids drawn at 30% probability, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Co(1)–C(11): 2.066(3); Co(1)–C(31): 2.075(4); Co(1)–N(1): 2.117(3); Co(1)–N(2): 2.108(3); N(1)–Co(1)–N(2): 127.32(15); C(11)–Co(1)–C(31): 96.20(11).

three measurements at different concentrations). Despite the relatively large error margin, this falls squarely in the range expected for high-spin Co^{II} (4.3-5.2¹⁴). Third, hydrolysis of an NMR sample containing the internal standard showed formation of Me₄Si and Py in the amounts expected for $(Py)_2CoR_2$. Finally, the presence of a transferable CoR_2 fragment was demonstrated by the reaction with TMEDA to give the known⁷ complex (TMEDA) CoR_2 . On treating $(Py)_2CoR_2$ with excess TMEDA in pentane, the reaction did not immediately go to completion, but evaporation of all solvents and crystallization from pentane containing a small amount of extra TMEDA resulted in formation of bluishpurple crystals of (TMEDA)CoR₂; the structure was confirmed by single-crystal X-ray diffraction (see Figure S1). This two-step synthesis has a considerably higher yield (57%) based on (Py)₄CoCl₂) than the procedure described by Hay-Motherwell.⁷ The ¹H NMR resonances of the TMEDA CH₂ and CH₃ groups overlap (Figure 1B: b,c), but the signals have very different linewidths and can be separated by deconvolution.

Structure of $(Py)_2Co(CH_2CMe_2Ph)_2$. While the abovementioned characterization data leave little doubt about the constitution of $(Py)_2CoR_2$, the lack of structural data is unsatisfactory. Since Cámpora did succeed in obtaining crystals of $(Py)_2FeR'_2$ ($R' = CH_2CMe_2Ph$),⁴ we decided to attempt synthesis of the Co analogue from $(Py)_4CoCl_2$ and R'MgCl. This reaction was found to suffer from a few complications. According to ¹H NMR, the hopedfor product $(Py)_2CoR'_2$ is indeed formed (see Table 1 and





Figure S3), but its formation is relatively slow and the product decomposes in a few hours at room temperature in solution. Also, the presence of pyridine induces disproportionation of the Grignard reagent to give a complex we assume to be (Py)₂MgR'₂, with solubility properties very similar to those of (Py)₂CoR'₂. Several crystallization attempts therefore produced mixtures of near-colorless $(Py)_2MgR'_2$ crystals and green-black blocks of $(Py)_2CoR'_2$. We eventually found conditions that lead to formation of fairly pure (by ¹H NMR) (Py)₂CoR'₂, albeit in low yield (20%). Even in the solid state, (Py)₂CoR'₂ was found to decompose in about a day at room temperature. A fragment broken from a green-black $(Py)_2CoR'_2$ crystal was used for a single-crystal structure determination. The quality of the data is not very high due to decay of the crystal during the measurement (see Experimental Section for details). Nevertheless, the results unambiguously show the connectivity expected for (Py)₂CoR'₂ (Figure 2). Both the unit cell dimensions and the molecular conformation are very similar to those reported by Cámpora for the Fe analogue;⁴ the most notable differences between the two structures are in the CMC angle (about 5° smaller for Co) and the NMN angle (about 5° larger for Co). We do not at present have a good explanation for the lower stability of (Py)₂CoR'₂ compared to $(Py)_2CoR_2$, but the analogous Fe complexes seem to follow the same stability order.

Exchange with DIMPY and Related Ligands. In the context of our study of ligand effects,¹⁵ we are interested in preparing variations on the DIMPY theme with varying steric and σ -donor/ π -acceptor properties. To assess the potential of (Py)₂CoR₂ and (TMEDA)CoR₂ as sources of the CoR₂ fragment, we studied transfer to ligands 1–6 (Scheme 1). Ligands 1–4 are electronically similar to "standard" DIMPY ligand 7 but are less effective at shielding the metal center. Of the remaining two variations, fluorinated ligand 5 emerged as being a clearly better π -acceptor than 1, but also a weaker σ -donor,¹⁵ whereas PyBOX ligand 6¹⁶ is a much poorer π -acceptor¹⁷ than 1–4.

Both $(Py)_2CoR_2$ and $(TMEDA)CoR_2$ reacted rapidly with both 1 and 2 to give deep purple, diamagnetic *monoalkyl* complexes as the sole observed products. They were easily

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⁽¹⁷⁾ Calculated ligand parameters for **6** (following the procedure of ref 15): $\sigma = +1.83$, $\pi = +12.21$ ($E_{\text{reorg}} = -10.01$). These values are relative to ligand **1**; positive values indicate poorer donor or acceptor properties.



Figure 3. X-ray structure of (1)CoR (thermal ellipsoids drawn at 30% probability, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Co(1)-N(1): 1.834(2); Co(1)-N(2): 1.9165(15); C(1)-N(2): 1.330(2); C(1)-C(2): 1.434(3); Co(1)-C(14): 1.964(3); N(1)-Co(1)-N(2): 80.63(5); Si-C(14)-Co(1): 128.55(15); N(1)-Co(1)-C(14): 165.07(10).

identified by their characteristic ¹H NMR signals (Py H4 at 10.1 ppm, N=CMe at -1.2 ppm¹⁸). Since synthesis of (TMEDA)CoR₂ requires an additional step, $(Py)_2CoR_2$ is the reagent of choice here. The complex formed from 2 could not be obtained in crystalline form, but (1)CoR crystallizes well; the X-ray structure is shown in Figure 3. It is rather similar to the previously reported complex of 7:^{6a} the Co1-N1, C1-C2, and C1-N2 bond lengths in (1)CoR are virtually identical to the corresponding distances in (7)CoR, while the Co-C14 bond in (1)CoR is about 0.02 Å shorter, perhaps reflecting the lower steric pressure in the dimethylphenyl-substituted ligand. In both complexes, the alkyl carbon is bent out of the CoN₃ plane by a very similar amount (trans NCoC angle close to 165°). This is most likely to mitigate repulsion between the bulky trimethylsilyl group and the substituent aryl groups since (7)CoMe has a virtually linear NCoC arrangement.66

Encouraged by the clean reactions with 1 and 2, we also attempted transfer to the much more open ligands 3 and 4. (TMEDA)CoR₂ reacts with 3, and ¹H NMR spectra of the reaction mixtures (Figure S4A) indicated fairly clean formation of (3)CoR, with the expected characteristic signals for the pyridine *H4* (9.79 ppm) and imine *Me* (-1.10 ppm).¹⁸ The solutions show some stability (days), but all attempts at workup led to decomposition. ¹H NMR spectra obtained for the reaction of (Py)₂CoR₂ with 3 also indicated formation of a single diamagnetic Co¹ alkyl complex, but interestingly enough the chemical shifts are quite different from those obtained using (TMEDA)CoR₂; in particular, the characteristic signals at 9.79 and -1.10 ppm are absent (Figure S4B,C). Also, the chemical shifts observed this way vary depending on the (Py)₂CoR₂:3 ratio used and on the absolute concentration. We speculate that what is formed in this case might be a labile pyridine adduct (3)(Py)CoR in dynamic equilibrium with (3)CoR (*vide infra*). In any case, reaction mixtures obtained from $(Py)_2CoR_2$ and 3 slowly deposit black insoluble material and no products could be isolated from them.

As for 3, attempts to isolate well-defined complexes of 4 failed. Therefore, these reactions were monitored by ¹H NMR. The cleanest spectra were obtained using an excess of the cobalt dialkyl precursor. Reaction of (TMEDA)CoR2 with 4 produced the signals expected for (4)CoR: pyridine H4 at 9.74 ppm, imine Me at -0.64 ppm. Like for 3, reaction of 4 with excess $(Py)_2CoR_2$ gave signals consistent with a single Co^I alkyl, but at different chemical shifts than for the TMEDA reaction and dependent on reactant ratio and concentration (Figure S5B,C). In support of our hypothesis of pyridine complexation to the product, addition of excess pyridine to the (TMEDA)CoR₂ + 4 reaction mixture resulted in signals similar to those observed for $(Py)_2CoR_2 + 4$ (Figure 5D). Thus, it appears that the decreased steric shielding of ligands 3 and 4 (compared to 1 and 2) does not hinder formation of low-spin Co^I complexes but leads to a significant decrease of their stability.

For fluorinated ligand **5**, we expected easy formation of a highly stabilized Co^I alkyl. A description of the (previously unpublished) synthesis of **5** was kindly provided by Jon M. Malinoski (Brookhart group, UNC Chapel Hill)¹⁹ and is included in the Experimental Section; the structure of the ligand was confirmed by an X-ray structure determination (Figure 4). Unfortunately, ligand exchange was not very successful. With (TMEDA)CoR₂, not much reaction was observed within 2 h of mixing; on longer standing, the spectra broadened and a black solid precipitated. With excess (Py)₂CoR₂, ¹⁹F NMR spectra

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Figure 4. X-ray structure of 5 (30% thermal ellipsoids; hydrogen atoms omitted for clarity).



Figure 5. ¹H NMR spectrum of "(6)CoR₂", still containing some (TMEDA)CoR₂ (see text).

obtained immediately after mixing showed formation of a single main diamagnetic product as well as remaining free ligand (Figure S6B), and the corresponding ¹H NMR spectra (Figure S7B) showed upfield peaks compatible with formation of a diamagnetic Co^I alkyl species and Me₄Si. Even on standing, the free ligand did not completely disappear, but spectra became broader as a black solid precipitated (Figure S6C). On hydrolysis of the reaction mixture, the diamagnetic product was mostly converted back into the free ligand (Figure S6D). It seems likely that this diamagnetic product is (5)CoR or a pyridine adduct of it. In any case, the better π -acceptor ability of ligand 5 does not seem to translate into easier formation of a stable Co^I alkyl.

For weak π -acceptor ligand **6**, formation of Co¹ should be more difficult, and we hoped this might allow isolation of stable *dialkyl* complexes, the presumed intermediates before loss of an alkyl group. Unfortunately, the reaction of **6** with (Py)₂CoR₂ was found to be far from clean. A cleaner reaction was observed with (TMEDA)CoR₂, although this turned out to be an equilibrium with an equilibrium constant of 0.9(1).²⁰ In the equilibrium mixture, the ¹H NMR signals of free **6** are sharp, but those of free TMEDA are broadened, presumably due to exchange with (TMEDA)-CoR₂ (Figure 5).²¹ The equilibrium mixture was fairly stable at -35 °C but decomposed in hours at room temperature.

Choice of Computational Method. DFT is the only practical method for studying transition metal complexes of the type described here. The main choices to be made are basis set and functional. We decided to use the modest SV(P) basis for initial geometry optimizations and vibrational analyses, and the larger TZVP basis for reoptimization and improved

⁽²⁰⁾ See the Supporting Information for estimation of the K value.

⁽²¹⁾ Exchange broadening, if any, of (TMEDA)CoR₂ would not be detectable because its line width is completely dominated by paramagnetic broadening. The broadening of free TMEDA may have contributions from both standard exchange and paramagnetic relaxation.

energies. Since the reactions we are studying involve changes in spin state, different functionals can be expected to produce rather different results.²² In particular, "pure" functionals such as BP86 tend to favor low-spin states, while hybrid functionals such as B3LYP often favor high-spin states. There is, in general, no functional that can be expected to always produce accurate spin-state energy differences. For a series of cyclopentadienylcobalt carbonyl complexes, Gandon et al recently found that BP86 gave results close to experiment, whereas B3LYP incorrectly predicted the triplet state to be much too stable.²³ In contrast, in a study of (DIMPY)FeR₂ complexes²⁴ experimentally found to be high-spin, even b3-lyp put the high-spin state barely above the intermediate-spin state, and pure functionals gave a very definite preference for lower spin states.

To cover our bases, we explored the chemistry of our Co^I and Co^{II} alkyls with Turbomole²⁵ using both pure (b-p) and hybrid (b3-lyp) functionals (b-p and b3-lyp are similar to the Gaussian BP86 and B3LYP functionals, respectively, but use VWN(V) instead of VWN(III) for the correlation part of the functional^{26,27}). The results showed that, within the highspin state, the two functionals behave rather similarly. However, the predictions diverge for low-spin (DIMPY)-CoR₂ and (PyBOX)CoR₂. At the b3-lyp level, these are somewhat higher in energy than the high-spin states, which leads to predicted ligand exchange equilibria in agreement with experiment (vide infra). With the b-p functional, however, the low-spin states of both (DIMPY)CoR2 and (PyBOX)CoR₂ are much lower than the high-spin states, leading to equilibrium predictions incompatible with experiment. In addition, paramagnetic NMR shifts using b3-lyp were found to agree fairly well with experiment for these systems, while the b-p predictions are consistently further off. For these reasons, we only present the b3-lyp results here (the b-p results are included in the ESI), without implying that b3-lyp would in general be better for predicting spinstate energy differences.

Paramagnetic NMR Shifts. The NMR signals of Co^{II} dialkyls are all broadened and show strong paramagnetic shifts. The only "tool" for assignment is the integral, and that is not always enough. Therefore, we used computational methods to predict the paramagnetically shifted signals and support the assignments. The observed chemical shift can be written as²⁸

$$\delta^{\rm obs} = \delta^{\rm orb} + \delta^{\rm FC} + \delta^{\rm PC} \tag{1}$$



Figure 6. Comparison of calculated (B3LYP: $\delta^{\text{orb}} + \delta^{\text{FC}}$ only) and observed ¹H NMR chemical shifts (the solid line represents the ideal $\delta^{\text{obs}} = \delta^{\text{calc}}$ relation).

The reference shift δ^{orb} was calculated using Gaussian 03²⁹ (B3LYP/TZVP), the pseudocontact term δ^{PC} was neglected, and the Fermi contact term δ^{FC} was calculated according to eq 2,³⁰ where the isotropic hyperfine coupling A_{iso} was calculated with ORCA³¹ (B3LYP/TZVP).

$$\delta^{\rm FC} = A_{\rm iso} \frac{g_{\rm e} \beta_{\rm e} S(S+1)}{g_{\rm N} \beta_{\rm N} 3kT} \tag{2}$$

For (Py)₂CoR₂, (Py)₂CoR'₂, and (TMEDA)CoR₂ the agreement (Figure 6) is seen to be quite good (correlation coefficient of 0.9927) and supports our assignment in Table 1 (although the assignments for the phenyl *o* and *m* hydrogens of (Py)₂CoR'₂ might well be switched). Encouraged by this, we also estimated the shifts for (6)CoR₂, for which we do not know the structure. It is not *a priori* obvious what hapticity (κ^2 or κ^3) and spin state should be expected for this complex. Calculations using the pure functional b-p put the low-spin (LS) κ^3 structure about 10 kcal/mol *below* the high-spin (HS) κ^2 structure, while the hybrid functional b3-lyp predicts the high-spin κ^2 structure to be lowest, with LS κ^3 about 10 kcal/mol *higher* in energy. The calculated NMR data (Table S2) are much more consistent with a HS ground state and fast

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 Table 2. Calculated Free Energy Differences^a for Ligand

 Exchange Reactions (kcal/mol)

	R		
	Me	CH ₂ SiMe ₃	
$(Py)_2CoR_2 + TMEDA \rightarrow$	-3.5	-1.4	
$(TMEDA)CoR_2 + 2 Py$ $(TMEDA)CoR_2 + 1 \rightarrow$	+7.0	+12.7	
$(1)CoR_2 + TMEDA$ $(TMEDA)CoR_2 + 6 \rightarrow$	-1.4	+2.8	
$(6)CoR_2 + TMEDA$			

^{*a*} Electronic energies calculated using b3-lyp/TZVP; ZPE, enthalpy and entropy corrections for 298 K, 1 bar, gas phase, taken from SV(P) calculations.

exchange between the two alternative κ^2 structures, i.e., with the b3-lyp predictions. In particular, the predicted chemical shift for the pyridine H4 proton is -134 ppm for HS κ^2 and +163 for LS κ^3 (observed: -66.5 ppm).

Ligand Exchange and Formation of Co^I Complexes. (Py)₂CoR₂ appears to be useful as a source of "CoR₂" in ligand exchange reactions, although some of these appear to be equilibria: the chelate effect (with TMEDA and 6) does not seem to be enough to drive reactions to completion. Calculations (Table 2) confirm that the Py/TMEDA ligand exchange reaction is close to thermoneutral. The b3-lyp results also predict the TMEDA/6 ligand exchange equilibrium to be close to thermoneutral ($\Delta G_{calc} = +2.8 \text{ kcal/mol}$), again in agreement with experiment ($\Delta G_{obs} \approx +0.1 \text{ kcal/mol}$),³² whereas exchange with 1 is considerably uphill ($\Delta G_{calc} = +12.7 \text{ kcal/mol}$).

Experimentally, ligand exchange leads to formation of Co^I complexes for 1 and 2, but not as easily for 6. A reasonable mechanism, compatible with our observations, would be initial formation of a $(\kappa^2-L)CoR_2$ complex, conversion to $(\kappa^3-L)CoR_2$, and loss of an alkyl radical; this path was examined in more detail for ligands 1 and 6 using DFT. Since $(Py)_2CoR_2$ and $(TMEDA)CoR_2$ both have $S = \frac{3}{2}$ but the final Co¹ complex is diamagnetic, a spin flip has to occur at some point, and this might be relevant to the reaction profile. Therefore, we located local minima for the various possible coordination geometries and spin states and also located a number of minimum-energy crossing points (MECP)^{33,34} between the $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states starting from points close to the κ^2 and κ^3 geometries of the DIMPY complexes. Spin flips turn out to be quite easy in these systems and do not represent significant barriers in the energy profile. The final calculated free energy profiles for ligands 1 and 6 in combination with $CoMe_2$ and CoR_2 fragments are shown in Figure 7. In all cases, the lowest energy path involves a spin flip at the $(\kappa^2-L)CoR_2$ stage. Forming LS (κ^3 -1)CoMe₂ is then favorable, but formation of LS (κ^3 -1)Co(CH₂SiMe₃)₂ is 10 kcal/mol less favorable, presumably for steric reasons. Loss of an alkyl is favorable for (κ^3-1) Co(CH₂SiMe₃)₂ because it relieves the steric pressure. In the reaction with **6**, formation of the κ^3 complex is even less favorable than with **1**. This may in part be due to steric constraints of the PyBOX ligand backbone. In any case, the net barrier to alkyl loss is seen to be significantly higher for **6** than for **1**, in agreement with the fact that we can observe a cobalt dialkyl complex of **6** but not of **1**.

The overall reaction HS- $(\kappa^2-L)CoR_2 \rightarrow LS-(\kappa^3-L)CoR + R \cdot$ is endergonic in all cases. However, alkyl radicals are extremely reactive and will react with anything they encounter, making alkyl dissociation effectively irreversible.

Ligand Effects on Co¹R Formation. The reactions of (Py)₂CoR₂ and (TMEDA)CoR₂ with DIMPY and PyBOX shed some light on the mechanism of Co¹ alkyl formation for DIMPY complexes. The original DIMPY ligands 1 and 2 are strong enough σ -donors to displace pyridine from $(Py)_2CoR_2$ (at least in equilibrium) and strong enough π acceptors to then promote homolysis of one Co-C bond.³⁶ With less shielding ligands such as 3 and 4, the same reactions probably occur, but the initially formed LCoR complexes decompose. With weaker σ -donor ligand 5, displacement of pyridine or TMEDA is slower, but the better π -acceptor qualities of this ligand do not lead to a stable, isolable Co¹ alkyl. With the weaker π -acceptor ligand 6, Co¹ is less stabilized and loss of alkyl does not occur immediately, although the observed decomposition of (6)CoR2 may still involve Co^I intermediates.

On the basis of the experimental and computational results described above, we arrive at a mechanistic proposal for the reaction of DIMPY ligands with "CoR₂" as summarized in Scheme 2, involving a ligand exchange equilibrium, easy spin flip, and finally irreversible loss of alkyl. Of course, variations where alkyl loss happens at the LS- κ^2 stage cannot be excluded at this point. As well, in reactions of (Py)₂CoR₂ the decomposition might involve pyridine adducts (L)(Py)CoR.

Conclusions

The only literature mention of a pyridine cobalt dialkyl complex dates back to 1967, when Matsuzaki and Sukawa reported (Py)₂CoMe₂ to be extremely unstable;³⁷ it was characterized only by EPR. We were, therefore, pleasantly surprised by the stability of the new complex (Py)₂Co-(CH₂SiMe₃)₂, which at this point is by far the most easily accessible Co^{II} dialkyl. Its availability will make it easier to do systematic comparisons of dialkyl derivatives along the series Mn,³⁸ Fe,⁴ Co, Ni,³⁹ and Zn.⁴⁰

⁽³²⁾ In contrast, b-p predicts the equilibrium to be strongly on the side of *low-spin* (κ^3 -6)CoR₂. If comparisons are restricted to the high-spin state, b3-lyp and b-p predictions are rather close.

⁽³³⁾ See e.g.: Harvey, J. N. Spin-Forbidden Reactions in Transition Metal Chemistry. In *Computational Organometallic Chemistry*; Cundari, T. R., Ed.; Marcel Dekker: New York, 2001.

⁽³⁴⁾ MECP were located between DFT configurations having $S_z = \frac{1}{2}$ and $\frac{3}{2}$. All are single-determinant functions and do not represent pure spin states. Some "low-spin states", in particular with the b3-lyp functional, show significant spin contamination ($\langle S^2 \rangle$ values between up to 1.8). The MECP, therefore, correspond to switches between virtually pure quartet states and mixtures of doublet and quartet, and the true crossing barriers might be higher. But even if the true crossing barriers were twice as high as the ones we calculate, spin flip would still be easy.

⁽³⁵⁾ Thermal corrections, including zero-point energy corrections, are not simple for crossing points. The MECP "free energies" in the profile were obtained by combining their electronic energies with the average of the thermal corrections for the HS and LS minima connected to the MECP.

⁽³⁶⁾ For the analogous Co–C homolysis in Co^{III} complexes, see e.g.: (a) De Bruin, B.; Dzik, W. I.; Li, S.; Wayland, B. B. *Chem.—Eur. J.* **2009**, *15*, 4312. (b) Li, S.; De Bruin, B; Peng, C.-H.; Fryd, M.; Wayland, B. B. J. *Am. Chem. Soc.* **2008**, *130*, 13373. Note that because of the strong pacceptor character of the DIMPY ligand, a picture involving electron transfer to the ligand prior to homolysis, i.e., involving Co^{III}, might actually have some validity.

^{(37) (}a) Matsuzaki, K.; Yasukawa, T. J. Phys. Chem. 1967, 71, 1160.
(b) We checked that our procedure does not work for the synthesis of (Py)₂CoMe₂, although color changes observed during the reaction suggest a transient cobalt dimethyl species may be formed at some stage.

⁽³⁸⁾ Alberola, A.; Blair, V. L.; Carrella, L. M.; Clegg, W.; Kennedy, A. R.; Klett, J.; Mulvey, R. E.; Newton, S.; Rentschler, E.; Russo, L. *Organometallics* **2009**, *28*, 2112.



Figure 7. Reaction profiles (ΔG , b3-lyp/TZVP, kcal/mol) for CoMe₂ and Co(CH₂SiMe₃)₂ fragments bound to ligands **1** and **6**. Points marked × are minimum-energy crossing points (MECP) between HS and LS states; the others are local minima. MECP free energies are estimated.³⁵ For ligand **6**, points marked κ^{2*} have the oxazoline ring with its oxygen atom toward Co.

Scheme 2. Proposed Mechanism for Formation of (DIMPY)CoR Complexes



(Py)₂CoR₂, is a new, easily accessible source of transferable "CoR₂". If its noncrystalline nature is an issue, or if the liberated Py can interfere with further chemistry, (Py)₂CoR₂ can be converted into crystalline (TMEDA)CoR₂, which is equally useful as a CoR₂ synthon. The structure of the related but less stable complex (Py)₂Co(CH₂CMe₂Ph)₂ was confirmed by X-ray diffraction. Transfer of the CoR₂ fragment to DIMPY-type ligands is not straightforward and illustrates the delicate interplay between σ -donation, π -back-donation, steric effects, and the choice of labile ligand in affecting the course of the reaction. DFT results indicate that high-spin states are preferred for all Co^{II} dialkyl complexes; spin flip, required at some point to eliminate R and form a low-spin Co^{I} monoalkyl, is predicted to be easy. Comparison of calculated and observed paramagnetic ¹H NMR shifts appears to be a useful tool in assigning spin states of complexes like (6)CoR₂ that cannot be obtained in pure form.

Experimental Section

General Procedures. All experiments were performed under an argon atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. Pyridine and tetramethylethylenediamine were obtained from Aldrich and dried by distillation from calcium hydride. Pentane, hexane, toluene, diethyl ether, tetrahydrofuran, benzene, and benzene- d_6 were distilled from sodium/benzophenone. LiCH₂SiMe₃ was purchased from Aldrich and crystallized from pentane at -35 °C. Anhydrous CoCl₂ and 2-methyl-2-phenylpropylmagnesium chloride solution (0.5 M in diethyl ether) were purchased from Aldrich and used as received. Ligands 1-3,⁴¹ 4,⁴² and 6^{16} were prepared according to published procedures.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All NMR shifts (δ , ppm) were referenced to the solvent (benzene- d_6 , ¹H NMR: C₆D₅H δ 7.16 ppm; ¹³C NMR: C₆D₆ δ 128.0 ppm; CDCl₃, ¹H NMR: CHCl₃ δ 7.26 ppm; ¹³C NMR: CHCl₃ δ 77.0 ppm). Data were collected at room temperature unless otherwise noted. Deconvolution and line width determination for broad peaks were done with the SpinWorks package.⁴³ Elemental analyses were done by Guelph Chemical Laboratories Ltd.

2,6-(CF₃CO)₂C₅H₃N. In a 250 mL three-necked flask with Ar connection, dropping funnel, and septum equipped with an internal temperature sensor was placed 5 g (21.1 mmol) of

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⁽⁴¹⁾ Fan, R.-Q.; Zhu, D.-S.; Mu, Y.; Li, G.-H.; Yang, Y.-L.; Su, Q.; Feng, A.-H. *Eur. J. Inorg. Chem.* **2004**, 4891.

⁽⁴²⁾ Lappalainen, K.; Yliheikkilä, K.; Abu-Surrah, A. S.; Polamo, M.; Leskelä, M.; Repo, T. Z. Anorg. Allg. Chem. 2005, 631, 763.

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2,6-dibromopyridine in 56 mL of diethyl ether and 44 mL of THF. The magnetically stirred mixture was cooled in a methanol/ liquid nitrogen cooling bath to an internal temperature of -95 °C (dibromopyridine starts to precipitate). Then 13.6 mL of 1.6 M n-BuLi in hexanes (21.6 mmol) was added in about 10 min, keeping the temperature of the mixture below -90 °C. A 3 mL amount of diethyl ether was used to rinse the wall of the dropping funnel, and this was added to the mixture. Warming of the mixture to -90 °C resulted in dissolution of the precipitated dibromopyridine, giving a clear yellow solution. After an additional 5 min of stirring at -90 °C, the mixture was cooled to -100 °C and 2.74 g (21.4 mmol) of methyl trifluoroacetate was added over 10 min, keeping the temperature below -90 °C. Some ether was used to rinse the funnel. The mixture was stirred for 20 min at -90 °C. then cooled to -113 °C, and 13.6 mL of 1.6 M n-BuLi was added while the temperature was kept below -100 °C. After 5 min of stirring, 2.8 g (21.8 mmol) of methyl trifluoroacetate was added while keeping the temperature below -100 °C.

The mixture was allowed to warm, and when it reached -60 °C, a mixture of 7 mL of 12 M HCl and 5 mL of water was added. The reaction mixture was then poured into a mixture of 25 mL of 12 M HCl and 150 mL of water. The organic layer was separated and dried with magnesium sulfate, and the solvent was evaporated *in vacuo*. The crude product was refluxed in rotary vane pump vacuum for 1 h (bath 120 °C, small flask, short condensor) and then solidified on cooling. Short-path distillation (the product solidifies in the receiver) gave 4.47 g (82%) of the colorless product, which according to NMR still contained ca. 14% of the monohydrate. This mixture was used without further purification for the synthesis of **5**.

¹H NMR (300.1 MHz, CDCl₃, 25 °C): δ 8.43 (2H, d, ³J 7.9 Hz, Py H3), 8.27 (1H, t, ³J 7.9 Hz, Py H4). ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ 179.7 (q, ²J_{CF} 35 Hz, C=O), 147.9 (Py C2), 139.2 (Py C4), 129.1 (Py C3), 116.4 (q, ¹J_{CF} 290 Hz, CF₃). ¹⁹F NMR (282.4 MHz, CDCl₃, 25 °C): δ –73.1.

Before refluxing and distillation, the crude mixture contained only a small amount of $2,6-(CF_3CO)_2C_5H_3N$; the main components were its bis(hemiketal) (mixture of two diastereomers), hemiketal/hydrate, bis(hydrate), monohemiketal, and monohydrate, causing the NMR spectra to look messy. Crystals of the bis(hydrate), suitable for X-ray diffraction, crystallized spontaneously from the THF solution of an NMR sample.

2,6-[2,4,6-Me₃C₆H₂N=C(CF₃)]₂C₅H₃N (5). (This synthesis does not require an inert atmosphere.) The crude bis-(trifluoroacetyl)pyridine mixture described above was dissolved in 50 mL of toluene, 4.3 g of 2,4,6-trimethylaniline and a small quantity of *p*-toluenesulphonic acid were added, and the orange mixture was refluxed in a Dean–Stark apparatus for 72 h. The toluene was removed using a rotary evaporator. The residue was crystallized from hexane/toluene (50 mL, ca. 2:1, 85 °C/RT) to give 6.23 g (78%) of yellow crystals. A crystal from this batch was used for X-ray structure determination.

¹H NMR (300.1 MHz, CDCl₃, 25 °C): δ 7.42 (1H, t, ³*J* 7.9 Hz, Py *H*4), 6.93 (2H, d, ³*J* 7.9 Hz, Py *H*3), 6.75 (4H, s, Ar *m*), 2.22 (6H, s, Ar *p*-*Me*), 1.90 (12H, s, Ar *o*-*Me*). ¹³C NMR (75.5 MHz, CDCl₃, 25 °C): δ 154.6 (q, ²*J*_{CF} 33 Hz, *C*=N), 149.1 (Py *C*2), 142.3 (Ar *i*), 136.6 (Py *C*4), 134.1 (Ar *p*), 128.8 (Ar *m*), 124.8 (Ar *o*), 124.2 (Py *C*3), 119.2 (q, ¹*J*_{CF} 280 Hz, *C*F₃), 20.6 (Ar *p*-*Me*), 17.5 (Ar *o*-*Me*). ¹⁹F NMR (282.4 MHz, CDCl₃, 25 °C): δ -68.6. Anal. Calcd for C₂₇H₂₅F₆N₃ (505.50): C, 64.15; H, 4.98; N, 8.31. Found: C, 64.34; H, 5.30; N 8.40.

(**Py**)₄**CoCl₂**. Anhydrous CoCl₂ (1.36 g, 10.4 mmol) was transferred into a 100 mL Schlenk tube, and 15 mL of pyridine was added. The resulting suspension of initially blue solid in a pink solution was stirred overnight at room temperature, during which the solid became pink. The solid was filtered off and dried *in vacuo*, giving 3.65 g (78%) of pink crude (Py)₄CoCl₂. Anal. Calcd for C₂₀H₂₀Cl₂CoN₄ (446.24): C, 53.83; H, 4.52; N, 12.56; Cl, 15.89. Found: C, 53.67; H, 4.85; N, 12.81; Cl, 16.10.

(Py)₂CoR₂. Pink (Py)₄CoCl₂ (0.32 g, 0.72 mmol) was transferred into a 50 mL Schlenk tube, and 10 mL of pentane was added to form a blue suspension. The resulting mixture was cooled to -70 °C and kept at this temperature for 20 min. LiCH₂SiMe₃ (0.136 g, 1.44 mmol) was weighed and dissolved in 10 mL of hexane; this solution was added dropwise to the above blue suspension at -70 °C. The color of the mixture changed to blue-green. It was kept at -70 °C for another 20 min and was then allowed to slowly (3 h) warm to room temperature. During this, the color first changed to red (around -10 °C), and then at around 0 °C most of the solid dissolved to form a yellow-green solution with some suspended white solid. This was stirred for another hour at room temperature and filtered through a glass frit. Solvents were removed in vacuo, leaving a thick bright green oil. Addition of a small amount of hexamethylbenzene as an internal standard allowed determination of the yield by NMR: 75%. For most subsequent experiments, a single portion of $(Py)_2CoR_2$ was prepared and used assuming this 75% yield.

¹H NMR (25 °C, benzene-*d*₆, 300 MHz): δ 114 (4H, $\Delta \nu_{1/2}$ 1600 Hz, Py *H*2), 38.4 (4H, $\Delta \nu_{1/2}$ 500 Hz, Py *H*3), 10.3 (18H, $\Delta \nu_{1/2}$ 80 Hz, Si*Me*₃), -8.5 (2H, $\Delta \nu_{1/2}$ 190 Hz, Py *H*4); C*H*₂(Co) not observed.

Evans Method for Determination of Magnetic Moment. ¹³ In a drybox, one drop of (Py)₂CoR₂ was dissolved in about 0.5 mL of C_6D_6 in a small vial, and 0.0253 g of C_6Me_6 (reference and internal standard) was added. The resulting green solution was diluted to 3.1 mL by adding C_6D_6 . Integration of the ¹H NMR spectrum showed the concentration of (Py)₂CoR₂ to be 0.22 mol/L; the chemical shift difference between C_6Me_6 in the paramagnetic solution and in pure C_6D_6 was found to be 9.14 ppm, implying a magnetic moment of 4.9 μ_B Two further experiments at different concentrations produced similar values (0.66 mol/L: 4.5 μ_B ; 0.052 mol/L: 5.0 μ_B); average 4.8(3) μ_B .

Hydrolysis. In a drybox, 0.158 g of (Py)₂CoR₂ and 0.053 g of C₆Me₆ were weighed into a small vial. Part of this sample was used for a ¹H NMR spectrum in C₆D₆. From the observed molar ratio of (Py)₂CoR₂ and C₆Me₆ (1.13:1, by integration), the purity was calculated to be 91%. To the NMR sample was added 0.05 mL of water, the resulting suspension was quickly filtered, and the ¹H NMR spectrum of the filtrate was recorded. The only visible signals were due to pyridine, tetramethylsilane, and hexamethylbenzene. The observed molar ratio of the Py, Me₄Si, and C₆Me₆ species in solution (1.97:2.12:1, by integration; expected 2.26:2.26:1) agreed reasonably well with the expected values for (Py)₂CoR₂, considering that some Py will remain coordinated to Co and/or stay in the water droplet and some Me₄Si will evaporate during filtration.

(TMEDA)CoR₂. (Py)₂CoR₂ (0.82 mmol, assuming 75% yield from (Py)₄CoCl₂; see above) was dissolved in 5 mL of pentane, and the green solution was cooled to -30 °C. TMEDA (10 equiv, 1.25 mL, 8.2 mmol) was slowly added at -30 °C, resulting in a color change to first red and then brown. After filtering, the solution was evaporated to dryness. The residue was dissolved in 2 mL of pentane, 1 drop of TMEDA was added, and the solution was cooled to -35 °C, depositing a dark solid. The cold liquid was pipetted off, and the solid was dried to give a purple-blue solid (0.22 g, 57% yield based on (Py)₄CoCl₂ or 76% yield based on (Py)₂CoR₂). Deep bluish-purple crystals suitable for X-ray diffraction were grown by cooling the saturated pentane solution at -35 °C overnight.

¹H NMR (25 °C, benzene-*d*₆, 300 MHz): δ 80 (4H, $\Delta \nu_{1/2}$ 600 Hz, CH₂N), 78 (12H, $\Delta \nu_{1/2}$ 350 Hz, NMe), 9.6 (18H, $\Delta \nu_{1/2}$ 70 Hz, SiMe₃); CH₂(Co) not observed.

 $(Py)_2CoR'_2$. A number of procedures were tried for the synthesis of this complex, but none gave a completely pure product. Procedure A below was used to generate the mixture of $(Py)_2MgR'_2$ and $(Py)_2CoR'_2$, from which a crystal was used for the X-ray structure determination mentioned in the text. Procedure B gave a better quality product for which the NMR spectrum could be assigned with some confidence.

Procedure A. Pink (Py)₄CoCl₂ (1.24 g, 2.78 mmol) was transferred into a 50 mL Schlenk tube, and 26 mL of dry diethyl ether was added to form a blue suspension. The resulting mixture was cooled to -50 °C. R'MgCl (11.8 mL of a 0.5 M solution in diethyl ether, 5.90 mmol) was added dropwise. The solution quickly turned green, and a white solid was formed. The stirred mixture was slowly (in 30 min) warmed to room temperature. Then 1.5 mL of dry pyridine was added, and the resulting green suspension was stirred at room temperature for another 30 min and filtered through a glass frit. The solvents were removed in vacuo, the residue was transferred into a drybox, dry pentane was added, and the suspension was filtered through glass wool. On standing overnight at -35 °C, the filtrate deposited whitish crystals of (presumably) (Py)₂MgR'₂ (see below), dark green blocks of (Py)₂CoR'₂, and some sticky dark oily droplets. A fragment of one of the dark green blocks was used for single-crystal X-ray structure determination. ¹H NMR of the deposited solids in C_6D_6 indicated the presence of both $(Py)_2MgR'_2$ and $(Py)_2CoR'_2$ (see below).

Procedure B. Pink (Py)₄CoCl₂ (0.69 g, 1.55 mmol) was transferred into a 100 mL Schlenk tube, and 26 mL of dry THF was added to form a blue clear solution. This was cooled to -50 °C, during which a pink solid precipitate formed. R'MgCl (2.8 mL of a 0.5 M solution in diethyl ether, 1.4 mmol) was added dropwise. The resulting mixture was warmed to around 0 °C in 1 h, during which it turned purplish and a white solid was formed. The solution was again cooled to -50 °C, and R'MgCl (3.2 mL of a 0.5 M solution in diethyl ether, 1.6 mmol) was added dropwise. The resulting suspension was stirred at -50 °C for 20 min and warmed to room temperature in 1 h, during which it turned green. Then 0.6 mL of dry pyridine was added, and the green mixture was cooled to -30 °C and concentrated to about 2 mL. A 20 mL portion of dry pentane was added, the solution was filtered through a glass frit, and the filtrate was cooled to -35 °C. Overnight, a dark and shiny solid crystallized; the mother liquid was pipetted off, leaving 0.15 g (20%) of reasonably pure (Py)₂CoR'₂. NMR samples always show some decomposition to diamagnetic compounds (pyridine, PhCMe₃), and within 4 h all signals due to $(Py)_2CoR'_2$ disappear.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; assignment tentative): δ 108 (4H, $\Delta \nu_{1/2}$ 5300 Hz, Py H2), 32.7 (4H, $\Delta \nu_{1/2}$ 1700 Hz, Py H3), 21.6 (12H, $\Delta \nu_{1/2}$ 270 Hz, CMe₂), 10.2 (4H, $\Delta \nu_{1/2}$ 160 Hz, Ar o), 7.4 (4H, $\Delta \nu_{1/2}$ 27 Hz, Ar m), 3.9 (2H, $\Delta \nu_{1/2}$ 17 Hz, Ar p), -8.1 (2H, $\Delta \nu_{1/2}$ 590 Hz, Py H4).

Formation of $(Py)_2Mg(CH_2CMe_2Ph)_2$. Under a nitrogen atmosphere, 5 mL of dry pyridine was dissolved in 15 mL of dry pentane, and 5 mL of 2-methyl-2-phenylpropylmagnesium chloride solution (0.5 M in diethyl ether) was added, resulting in precipitation of a white powder. The resulting yellow solution with white suspended solid was stirred for another 2 h at room temperature and filtered through a glass frit. The filtrate was evaporated to dryness, and the resulting yellow sticky oil was dissolved in toluene and layered with pentane at -35 °C overnight, forming a yellow crystalline solid (0.45 g, 80%).

¹H NMR (25 °C, benzene- d_6 , 300 MHz): δ 7.90 (d, 4H, J 4.0 Hz, Py H2), 7.78 (d, 4H, J 7.7 Hz, Ar o), 7.12 (t, 4H, J 7.7 Hz, Ar m), 6.99 (t, 2H, J 7.2 Hz, Ar p), 6.78 (t, 2H, J 7.4 Hz, Py H4), 6.41 (t, 4H, J 6.4 Hz, Py H3), 1.83 (s, 12H, Me), 0.77 (s, 4H, CH₂). ¹³C NMR (25 °C, benzene- d_6 , 75 MHz): δ 158.3 (Ar i), 148.82 (Py C2), 137.69 (Py C4), 127.80 (Ar m), 125.92 (Ar o), 124.21 (Py C4), 123.91 (Ar, p), 40.41 (CMe2), 36.62 (CMe2), 34.48 (CH2).

(1)CoR. (Py)₂CoR₂ (1.14 mmol assuming 75% yield from (Py)₄CoCl₂; see above) was dissolved in 8 mL of diethyl ether, and the green solution was cooled to -30 °C. Ligand 1 (0.39 g, 1.06 mmol) was dissolved in 20 mL of diethyl ether, and the clear yellow solution was slowly added into the above (Py)₂CoR₂ solution at -30 °C. After the addition, the solution (which had turned red) was allowed to warm to room temperature (around 0 °C the color changed to purple). After stirring for another

hour, the deep purple solution was filtered and the solvent was evaporated *in vacuo*. The residue was dissolved in 4 mL of diethyl ether/pentane (1:1), the solution was concentrated to 2 mL, 1 mL of hexane was added, and the mixture was cooled to $-35 \,^{\circ}\text{C}$ overnight. The purple mother liquor was decanted, and the residue was recrystallized from toluene (6 drops)/hexane (5 mL) to give shiny dark crystalline (1)CoR (0.23 g, 42%) suitable for X-ray diffraction.

¹H NMR (25 °C, benzene-*d*₆, 300 MHz): δ 10.08 (t, 1H, *J* 7.7 Hz, Py *H*4), 7.74 (d, 2H, *J* 7.7 Hz, Py *H*3), 7.36 (t, 2H, *J* 7.4 Hz, Ar *p*), 7.27 (d, 4H, *J* 7.4 Hz, Ar *m*), 2.12 (s, 12H, Ar *Me*), 0.81 (s, 2H, CoC*H*₂), -0.62 (s, 9H, Si*Me*₃), -1.26 (s, 6H, N=C*Me*). ¹³C NMR (25 °C, benzene-*d*₆, 75 MHz): δ 165.6 (N=C), 158.4 (Py C2), 156.0, 130.2, 129.1, 125.9, 123.3, 116.7, 23.8 (N=C*Me*), 19.5 (Ar *Me*), 3.8 (Si*Me*₃), -10.7 (br, CoC*H*₂). Anal. Calcd for C₂₉H₃₈CoN₃Si (515.65): C, 67.55; H, 7.43; N, 8.15. Found: C, 67.32; H, 7.14; N, 7.70.

(2)CoR. This reaction was carried out as described for 1, using 0.9 mmol of $(Py)_2CoR_2$ and 0.35 g (0.88 mmol) of 2. After evaporation of the solvents, the resulting thick purple oil was dissolved in pentane and filtered through glass wool. Slow evaporation produced a sticky product (0.26 g, crude yield: 56%). All attempts at crystallization failed.

¹H NMR (25 °C, benzene- d_6 , 300 MHz): δ 10.13 (t, 1H, J 7.0 Hz, Py H4), 7.79 (d, 2H, J 7.0 Hz, Py H3), 7.11 (s, 4H, Ar m), 2.37 (s, 6H, Ar *p*-Me), 2.16 (s, 12H, Ar *o*-Me), -0.60 (s, 9H, SiMe₃), -1.14 (s, 6H, N=CMe). The CoCH₂ signal could not be unambiguously assigned.

Reaction of (TMEDA)CoR₂ with 3. In a drybox, 5.2 mg (17 μ mol) of **3** was dissolved in benzene- d_6 and transferred into an NMR tube, and a solution of 6.2 mg of (TMEDA)CoR₂ (18 μ mol, 1.1 equiv) in benzene- d_6 was added. For the ¹H NMR spectrum, see Figure S4A.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; tentative assignments): δ 9.79 (t, 1H, J 7.4 Hz, Py H4), 8.17 (d, 4H, J 6.6 Hz, Ar o), 7.76 (d, 2H, J 7.2 Hz, Py H3), 7.35–7.43(m, 6H, Ar *m* and Ar p), 0.35 (s, 2H, CoCH₂), -0.64 (s, 9H, SiMe₃), -1.10 (s, 6H, N=CMe).

Reaction of (Py)₂CoR₂ with 3. In a drybox, about 59 μ mol of (Py)₂CoR₂ was dissolved in benzene- d_6 and 0.015 g (48 μ mol; 0.81 equiv) of **3** was added. A ¹H NMR spectrum recorded immediately afterward (Figure S4B,C) showed peaks that we tentatively assign in terms of formation of 1 equiv of Me₄Si and 1 equiv of (**3**)CoR or (**3**)(Py)CoR.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; tentative assignments): δ 8.71 (br, 1H, Py H4), 8.37 (br, Py H3), 7.00 (4H, Ph o), 6.91 (4H, Ph m), 6.82 (2H, Ph p), 0.85 (s, 6H, MeC=N), 0.45 (s, 2H, CoCH₂), 0.05 (s, 12H, Me₄Si), -0.50 (s, 9H, SiMe₃).

Reaction of (TMEDA)CoR₂ with 4. In a drybox, 6.8 mg of 4 (20 μ mol) was weighed and dissolved in benzene- d_6 , followed by addition of around 9.2 mg of (TMEDA)CoR₂ (26 μ mol, 1.3 equiv) in benzene- d_6 . A ¹H NMR spectrum recorded immediately (Figure S5A) showed peaks that could be tentatively assigned to (4)CoR.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; tentative assignments): δ 9.74 (t, 1H, *J* 7.4 Hz, Py *H*4), 7.40 (d, 2H, *J* 7.4 Hz, Py *H*3), 6.61 (s, 4H, PhC*H*2), -0.16 (s, 9H, Si*Me*₃), -0.64 (s, 6H, N=C*Me*).

Pyridine was added to this sample in small increments; this resulted in changes in shifts of the ¹H NMR signals attributed to the Co^I alkyl. Figure S5D shows the spectrum after addition of 3μ L of Py.

Reaction of $(Py)_2CoR_2$ **with 4.** In a drybox, about 6.8 mg (20 μ mol) of **4** was added to a solution of about 40 μ mol of $(Py)_2CoR_2$ in benzene- d_6 . A ¹H NMR spectrum recorded immediately afterward (Figure S5C) showed peaks that could be interpreted in terms of formation of 1 equiv of Me₄Si and 1 equiv of (4)CoR or (4)(Py)CoR.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; tentative assignments): δ 9.32 (t, 1H, J 6.6 Hz, Py H4), 7.54 (d, 2H, J 6.6 Hz, Py

	2,6-[CF ₃ C(OH) ₂] ₂ C ₅ H ₃ N ⋅ THF	5	(TMEDA)CoR ₂	(Py) ₂ CoR' ₂	(1)CoR
formula	$C_9H_7NO_4F_6\cdot C_4H_8O$	C ₂₇ H ₂₅ F ₆ N ₃	C14H38CoN2Si2	C ₃₀ H ₃₆ CoN ₂	C ₂₉ H ₃₈ CoN ₃ Si
mol wt	379.26	505.50	349.57	483.54	515.65
cryst syst	orthorhombic	tetragonal	monoclinic	triclinic	monoclinic
space group	Pcmn	I4 ₁	C2/c	$P\overline{1}$	$P2_1/m$ (No. 11)
a/Å	6.6689(3)	14.9916(10)	25.565(3)	11.8183(11)	7.6802(3)
b/Å	14.6578(8)	14.9916(10)	10.1487(10)	11.8294(12)	21.2770(10)
c/Å	17.1651(12)	11.1077(5)	17.3758(18)	12.1892(12)	8.5207(4)
a/deg	90	90	90	105.652(2)	90
β/\deg	90	90	100.104(6)	109.119(2)	99.1876(11)
γ/deg	90	90	90	108.825(2)	90
$V/Å^3$	1677.91(17)	2496.4(3)	4438.3(8)	1383.1(2)	1374.52(11)
Ź	4	4	8	2	2
$D_c/\mathrm{g}~\mathrm{cm}^{-3}$	1.501	1.345	1.046	1.161	1.246
abs coeff/mm ⁻¹	0.155	0.111	0.875	0.639	0.689
F000	776	1048	1528	514	548
index ranges	$-7 \le h \le 7$	$-17 \le h \le 17$	$-30 \le h \le 30$	$-14 \le h \le 14$	$-9 \le h \le 9$
8	$-17 \le k \le 17$	$-17 \le k \le 17$	$-12 \le k \le 12$	$-14 \le k \le 14$	$-25 \le k \le 25$
	$-20 \le l \le 16$	$-13 \le l \le 13$	$-20 \le l \le 21$	$-14 \le l \le 14$	$-10 \le l \le 10$
$2\theta_{\rm max}/{\rm deg}$	50	50	51	51	51
no. reflns	21 981	14675	13 479	10 195	9173
no. unique	1531	2193	4140	5166	2634
no. > 2σ	1116	1925	3163	4314	2459
GOF	1.086	1.074	1.054	1.088	1.075
no. params	126	167	186	324	174
$R(\hat{F}_{\alpha} > 4\sigma(F_{\alpha}))$	0.0623	0.0358	0.0374	0.0685	0.0379
R (all data)	0.0916	0.0455	0.0496	0.0772	0.0398
$w\hat{R}_2$ (all data)	0.1446	0.0853	0.1090	0.2060	0.1008
largest neak hole/e Å ⁻³	0.479 - 0.272	0.111 - 0.157	0.266 - 0.171	0.555 - 0.241	0.393 - 0.174

H3), 7.05-7.08 (br, Ar *o*), 6.90-6.93 (m, Ar *p* and Ar *m*), 6.32 (s, 4H, PhCH2), -0.15 (s, 6H, N=CMe), -0.24 (s, 9H, SiMe₃). CoCH2 could not be unambiguously assigned.

Figure S5B shows the results of a similar experiment using different concentrations of 4 and $(Py)_2CoR_2$, resulting in significantly different chemical shifts of the Co^I alkyl.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; tentative assignments): δ 8.94 (br, 1H, Py H4), 7.63 (br, Py H3), 6.95, 6.89 (br, 10H, Ph), 6.08 (4H, NCH₂), 0.25 (s, 6H, MeC=N), 0.12 (s, 2H, CoCH₂), 0.02 (s, 12H, Me₄Si), -0.32 (s, 9H, SiMe₃).

Reaction of (Py)₂CoR₂ with 5. In a drybox, 6.9 mg (17 μ mol) of 5 was weighed and dissolved in benzene- d_6 , followed by addition about 28 μ mol of (Py)₂CoR₂ in benzene- d_6 . ¹H and ¹⁹F NMR spectra were recorded immediately (Figures S6B, S7B) and showed the formation of Me₄Si and a small amount of a new diamagnetic compound, possibly (5)CoR or its Py adduct, as well as a large amount of both starting materials.

¹H NMR (25 °C, benzene- d_6 , 300 MHz; tentative assignments): δ 8.56 (d, 2H, J 7.9, Py H3), 2.36 (s, 6H), 0.34 (s, 2H, CoCH₂), -0.35 (s, 9H, SiMe₃). ¹⁹F NMR (282.4 MHz, benzene- d_6 , 25 °C): δ – 54.1.

On standing, a black solid precipitated from the sample. A spectrum (Figure S6C) recorded after 2 h still showed the presence of unreacted starting materials, although the amount of free 5 had decreased. Then 0.5 mL of water was injected, and after separation of layers spectra taken of the benzene- d_6 layer showed mainly free 5 (Figure S6D).

Formation of (6)CoR₂. (TMEDA)CoR₂ (0.082 g, 0.23 mmol) was dissolved in 2 mL of benzene and cooled to -35 °C, and 0.06 g (0.23 mmol) of 6 in 2 mL of benzene was added. After warming to room temperature, the resulting blue solution was stirred for 10 min and filtered through glass wool, solvents were evaporated, 2 mL of pentane was added, and the solution was again filtered through glass wool. Cooling failed to produce crystals, so the solvents were evaporated and the crude product (a mixture of (6)CoR₂ and (TMEDA)CoR₂, see text and Figure 5) was characterized by ¹H NMR.

¹H NMR (25 °C, benzene-*d*₆, 300 MHz): δ 44.4 (2H, br, $\Delta \nu_{1/2}$ 80 Hz, Py H3), 21.8 (18H, br, $\Delta \nu_{1/2}$ 120 Hz, Si*Me*₃), -5.6 (4H, br, CH₂O), -16.9 (12H, br, $\Delta \nu_{1/2}$ 110 Hz, C*Me*₂), -66.5 (1H, br, Py H4). X-ray Structure Determinations (see also Table 3). General Procedures. All measurements were done using Mo K α radiation (0.71073 Å). Semiempirical absorption was done using SADABS.⁴⁴ Structures were refined using full-matrix least-squares refinement on F^2 with SHELXL97;⁴⁵ hydrogen atoms were placed at calculated positions and refined in riding mode. Structures were checked for solvent-accessible voids with PLATON.⁴⁶

2,6-[CF₃C(OH)₂]₂C₅H₃N. A transparent regular platelet (approximately $0.3 \times 0.2 \times 0.1$ mm) was glued on a thin glass fiber. Data were collected at 208 K on a Nonius KappaCCD diffractometer with area detector φ and ω scans. The structure was solved using CRUNCH.⁴⁷ There is some minor rotational disorder in the CF₃ groups, resulting in somewhat larger anisotropic thermal displacement parameters. A cocrystallized THF solvent molecule is situated in a mirror plane, implying the presence of some disorder, which is reflected in large thermal parameters perpendicular to the plane of the molecule. This disorder could not be described adequately, and attempts to do so resulted in physically unacceptable geometrical parameters. A thermal ellipsoid plot is provided in the Supporting Information.

2,6-[2,4,6-Me₃C₆H₂N=C(CF₃)]₂C₅H₃N (5). A transparent light yellow crystal fragment (approximately 0.2 mm in all directions) was glued on a thin glass fiber. Data were collected at room temperature on a Nonius KappaCCD diffractometer with area detector φ and ω scans. The structure was solved using CRUNCH.⁴⁷

(1)CoR. A deep purple crystal fragment (ca. $0.6 \times 0.2 \times 0.1 \text{ mm}$) was mounted in a thin-walled glass capillary. Data were collected at 293 K on a Bruker 4-circle diffractometer with APEX detector. The crystal system and space group were

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determined from the cell metric and systematic absences. Data integration was performed using SAINT.⁴⁸ The structure was solved by the Patterson method with SHELXS97.⁴

(TMEDA)CoR₂. The procedure was the same as for (1)CoR. A deep bluish-purple crystal fragment (ca. $0.5 \times 0.2 \times 0.15$ mm) was mounted in a thin-walled glass capillary. Data were collected at 293 K on a Bruker 4-circle diffractometer with APEX detector. The crystal system and space group were determined from the cell metric and systematic absences. Data integration was performed using SAINT.⁴⁸ The structure was solved by the Patterson method with SHELXS97.⁴⁹ A thermal ellipsoid plot is provided in the Supporting Information. This is not a new structure: the structure of the complex was originally determined by Hay-Motherwell,⁷ and we find the same unit cell and coordinates. However, these authors did not report any characterization data other than the X-ray structure, so we used our structure determination as confirmation of the identity of the complex.

 $(\mathbf{Py})_2 \mathbf{CoR'}_2$. A large irregular crystal fragment (ca. $0.6 \times 0.5 \times$ 0.4 mm) was broken off an even larger block of green-black $(Py)_2CoR'_2$, picked from the results of a crystallization attempt (nearly colorless crystals of $(Py)_2MgR'_2$ were also present). The fragment was mounted in a thin-walled glass capillary. Data were collected using a 0.30° scan width, a 15 s scan time, and full-sphere coverage. The large scan width and fast scan time, as well as the large size of the crystal, had been chosen to allow rapid data collection, since Cámpora reported that the iron analogue decayed during data collection. Indeed, after about 75% of the full-sphere data were collected the crystal had visibly changed shape and did not diffract any more. Analysis of the diffraction data showed that at completion of the first hemisphere of data decay was less than 15%. Therefore, only this first hemisphere of data was processed and used in the refinement. The data integration was performed using SAINT⁴⁸ with decay correction, and absorption correction was performed by SADABS. The structure was solved by the Patterson method using SHELXS97.49 Even though the final thermal parameters and error margins look acceptable, the data should be treated with caution because of the crystal decay during data collection.

Computational Methods. All geometry optimizations were carried out with Turbomole²⁵ using the SVP⁵⁰ and TZVP⁵¹

basis sets and the functionals $b3-lyp^{52}$ and $b-p^{53}$ (the latter with the RI approximation) in combination with an external optimi-zer (PQS OPTIMIZE⁵⁴ for minima, BOptimize⁵⁵ for MECP³³). All calculations used the spin-unrestricted formalism, with $S_z =$ $\frac{1}{2}$ (Co^{II} HS), $\frac{1}{2}$ (Co^{II} LS), or 0 (Co⁽⁰⁾ LS). Vibrational analyses were carried out for all stationary points to confirm their nature and also to calculate thermal corrections (enthalpy and entropy, gas phase, 298 K, 1 bar) and obtain free energies using the standard formulas of statistical thermodynamics.⁵⁶ For the TZVP/b3-lyp calculations, calculation of analytical Hessians proved to be prohibitively expensive, so we here combine the TZVP optimized electronic energies with SV(P)-level thermal corrections evaluated at the SV(P) optimized geometries.

The σ - and π -parameters of ligand **6** were generated according to the procedure in our previous paper.¹⁵ Calculations of the orbital contributions δ^{orb} to the chemical shift were done using Gaussian 03²⁹ (B3LYP functional, TZVP basis set, GIAO method;⁵⁷ same S_z as used for geometry optimizations). EPR hyperfine couplings used to estimate Fermi contact shifts δ^{FC} (eq 2) were calculated⁵⁸ using the Orca program³¹ (B3LYP functional, TZVP basis set).

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Supporting Information Available: Data for calculation of the equilibrium constant involving TMEDA/6 exchange; thermal ellipsoid plots for 2,6-[(HO)₂C(CF₃)]₂C₅H₃N and (TMEDA)-CoR₂; coordinates (xyz files) and energies for calculated structures; X-ray crystallographic information (cif file) for the five structure determinations described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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