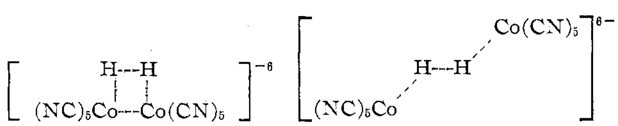
TABLE II
KINETIC DATA

Temp, °C	H_2 partial pressure, atm	Initial soln compn, *M*: $10^3[H_2]$	$10^3[Co(CN)_5^{3-}]$	$10^3[CN^-]$	$10^3[OH^-]$	Ionic strength, *M*	10^2k_{obsd}, M^{-1} sec^{-1}	*k*, M^{-2} sec^{-1}
25	3.37	2.59	3.0	3.0	0.5	0.10	21.6	41
25	0.97	0.76	6.0	6.0	0.5	0.10	5.5	36
25	1.67	1.29	6.0	6.0	0.5	0.10	10.1	39
25	3.37	2.59	6.0	6.0	0.5	0.10	21.3	41
25	6.8	5.18	6.0	6.0	0.5	0.10	41.1	39
25	10.2	7.76	6.0	6.0	0.5	0.10	63.8	41
25	3.37	2.59	6.0	6.0	0.1	0.10	21.3	41
25	3.37	2.59	6.0	6.0	10	0.10	21.2	41
25	3.37	2.59	6.0	6.0	40	0.10	21.0	40
25	3.37	2.59	6.0	6.0	58	0.10	21.5	41
25	3.37	2.59	6.0	0.6	0.5	0.10	21.6	41
25	3.37	2.59	6.0	1.5	0.5	0.10	21.6	41
25	3.37	2.59	6.0	3.0	0.5	0.10	21.7	41
25	3.37	2.59	6.0	10	0.5	0.10	21.0	40
25	3.37	2.59	6.0	40	0.5	0.10	21.3	41
25	3.37	2.59	6.0	64	0.5	0.10	21.5	41
25	3.37	2.59	6.0	6.0	0.5	0.043	6.1	12
25	3.37	2.59	6.0	6.0	0.5	0.068	12.2	23
25	3.37	2.59	6.0	6.0	0.5	0.143	33.1	63
25	3.37	2.59	6.0	6.0	0.5	0.243	68.0	131
0	3.41	3.26	6.0	6.0	0.5	0.10	29.5	45
15	3.39	2.85	6.0	6.0	0.5	0.10	24.2	42
35	3.33	2.50	6.0	6.0	0.5	0.10	19.0	38

This situation parallels that prevailing in the well-known reaction $H_2 + I_2$ (or 2I) → 2HI, where the path long designated as "bimolecular" has recently been demonstrated to be, in fact, termolecular.[13] The distinction between these two alternatives and between the corresponding alternatives (*i.e.*, whether or not $Co_2(CN)_{10}^{6-}$ is an intermediate) in the present reaction is presumably linked to the most favorable configurations (notably the degrees of residual I---I or Co---Co bonding) of the transition states of these reactions. Thus $Co_2(CN)_{10}^{6-}$ is likely to lie along the most favorable path for the formation of a transition state resembling I (*i.e.*, stabilized by residual Co–Co bonding) but not of a transition state resembling II. The latter situation apparently prevails in the case of the H_2–I_2 reaction and may well apply also in the present case where it would appear to be favored at least on steric grounds.



I II

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(12) The rapid "reversible" transformation of the green $Co(CN)_5^{3-}$ to the intensely violet dimer $Co_2(CN)_{10}^{6-}$ (the salts of which are well known) is readily detected visually as the concentrations of aqueous $Co(CN)_5^{3-}$ solutions are increased, particularly at low temperatures (∼0°). Attempts to study this reaction quantitatively were unsuccessful because of the instability of the solutions with respect to decomposition by reaction 3 under the conditions where reaction 6 is shifted measurably toward the right. Under the conditions of our hydrogenation experiments equilibrium 6 lay far to the left and the concentration of $Co_2(CN)_{10}^{6-}$ in solution was negligible.

(13) J. H. Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

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Contact Shift Studies and Spin Delocalization in Cobalt(I)–Tris(2,2′-bipyridine) Complexes

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There has been considerable interest lately in the use of nmr contact shifts to investigate the nature of the metal–ligand bond in substituted and unsubstituted tris (2,2′-bipyridine) complexes of first-row transition metals. The proton nmr contact shift data for Co(II),[2] Ni(II),[2,3] Cr(II),[4] and Fe(III)[4,5] have been reported. We report here the data for the Co(I) complexes.

Observed proton nmr contact shifts may arise from either a Fermi contact interaction or a dipolar interaction.

The Fermi contact interaction arises from a coupling of the delocalized electron spin and the nuclear spin. The relationship between the contact shift, $\Delta\nu$, and the hyperfine coupling constant A, in gauss, is then given by the modified Bloembergen equation[6]

$$\frac{\Delta\nu}{\nu_0} = -\frac{A g_{av}^2 \beta_e^2 S(S+1)}{g_N \beta_N 3kT} \qquad (1)$$

(1) Author to whom correspondence should be addressed.
(2) M. L. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2196 (1968).
(3) M. L. Wicholas and R. S. Drago, *ibid.*, **90**, 6946 (1968).
(4) G. N. La Mar and G. R. Van Hecke, *ibid.*, **91**, 3442 (1969).
(5) D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **41**, 908 (1964).
(6) N. Bloembergen, *ibid.*, **27**, 595 (1957).

We have defined these symbols and those in eq 2, *vide infra*, in a previous publication[7] and discussed them in detail there. An analysis of this Fermi contact interaction may yield useful information regarding the electronic structure of the complex.

The dipolar interaction couples the magnetic moments of the proton and the electron and gives rise to "pseudo-contact shifts." This occurs under conditions where there is a proper combination of geometric factors and magnetic anisotropy. This expression[8,9] is given by

$$\frac{\Delta\nu_i}{\nu_0} = -\frac{\beta_e^2 S(S+1)}{3kT}\frac{(3\cos^2\chi - 1)}{r_i^3}F(g_{||}, g_{\perp}) \quad (2)$$

More detailed descriptions of the theory and interpretation of nmr contact shifts have been given elsewhere.[10,11]

Previous studies[2-4] have shown that both σ- and π-delocalization mechanisms are important, to varying degrees, with different metals in complexes of this type. It was of interest to us to prepare and study the Co(I) complexes which are isoelectronic (d^8) with the previously reported Ni(II) complexes in order to compare the relative magnitudes of σ and π bonding.

Experimental Section

Preparation of Compounds.—Both $[Co^{II}(bipy)_3](ClO_4)_2$ and $[Co^{II}(4,4'\text{-}(CH_3)_2bipy)_3](ClO_4)_2$ (bipy = 2,2′-bipyridine) were prepared following the method of Burstall and Nyholm.[12] The carbon, hydrogen, and nitrogen analyses for these compounds and the 4,4′-$(CH_3)_2$bipy are given below. *Anal.* Calcd for $[Co(C_{10}H_8N_2)_3](ClO_4)_2$: C, 49.60; H, 3.33; N, 11.57. Found: C, 49.19; H, 3.46; N, 11.22. Calcd for $[Co(C_{12}H_{12}N_2)_3](ClO_4)_2$: C, 53.34; H, 4.48; N, 10.37. Found: C, 53.43; H, 5.25; N, 10.69. Calcd for $C_{12}H_{12}N_2$: C, 78.18; H, 6.58; N, 15.20. Found: C, 77.96; H, 6.42; N, 15.70.

The Co(I) complexes were prepared by modifying the methods of Waind and Martin[13] and Maki, *et al.*[14]

All procedures were performed under oxygen-free nitrogen. About 0.1 g (~0.14 mmol) of $[Co(L\text{-}L)_3](ClO_4)_2$ (L-L = bipy or 4,4′-$(CH_3)_2$bipy) was dissolved with stirring in 20 ml of oxygen-free ethanol. To this solution 0.05 g of the ligand (~0.3 mol of bipy or 4,4′-$(CH_3)_2$bipy) and 0.17 g of $NaBH_4$ (~4.5 mmol) were added with stirring. After about 1 min the yellow solution became green and then after 10 min the solution turned dark blue. Excess ligand was present to ensure the formation of the tris complex[15] and excess $NaBH_4$ was present to reduce any Co(II) moieties. A dark blue solid was precipitated when $NaClO_4$ or NaBr was added to this solution. Analyses of the air-sensitive Co(I) complexes were not obtained. Their presence in solution is shown by the uv and nmr spectral data, *vide infra*. These data also indicate that our solutions were not contaminated to any appreciable extent by the presence of Co(II) complex.

Reagents and Solutions.—2,2′-Bipyridine was purchased from Aldrich Chemical Co., Milwaukee, Wis. 4,4′-Dimethyl-2,2′-bipyridine was donated by Reilly Tar and Chemical Co., Indianapolis, Ind. Sodium borohydride was purchased from Fisher Scientific Co., Fair Lawn, N. J., and the ethanol was obtained from Commercial Solvents Corp., Chicago, Ill.

Nmr Spectral Measurements.—All nmr samples containing Co(I) were prepared and sealed under nitrogen. The ethanol, which was used as a solvent, was degassed by bubbling nitrogen through it for 24 hr. The nmr spectra were obtained on a Varian DA-60 spectrometer. The complexes were studied at a concentration of ~0.05 *M* in absolute ethanol solutions at 28°. The contact shifts, $\Delta\nu$, were referenced relative to the appropriate diamagnetic Fe(II) analog.

In order to oxidize the Co(I) species back to the Co(II) species, the nmr tube was exposed to oxygen by unsealing the tube and bubbling air through the solution. The dark blue solution immediately became yellow.

The hyperfine coupling constants were calculated by use of eq 1.

Uv Spectral Measurements.—All ultraviolet spectra were determined on either a Beckman DBG or a Cary recording spectrometer, Model 14. Ethanol was used as the solvent and purified as described, *vide supra*. A slight excess of ligand was present in solution to ensure the presence of the tris complex.[15]

Results

All of the complexed ligand signals appeared as broad singlets in the nmr spectra. The methyl protons were identified by integration of the spectra. The 3,3′- and 5,5′-hydrogen resonances were assigned by comparison with previously reported spectra.[2-4] In these cases, the contact shift for the 3,3′-hydrogens was always larger, as might be expected if a σ-delocalization mechanism is dominant.[3] Although it is not possible to assign the 3,3′- and 5,5′-hydrogen resonances unequivocally, one can make a probable assignment and this tentative assignment will not alter the conclusion to be drawn.

Despite repeated attempts and the relatively narrow line widths of the proton resonances in these Co(I) complexes (see Table I and Figures 1 and 2), we were unable to locate the 6,6′-hydrogen resonance for either of these complexes. Previous data[4] indicate that the line widths of the 6,6′-hydrogen signals should be approximately 10 times broader than those of the other protons. Apparently, the combination of broader line width and

TABLE I
NMR RESULTS

Compound	Group	δ,[a] Hz	$\Delta\nu$,[b] Hz	$\Delta\nu_{1/2}$,[c] Hz
$Co^I(bipy)_3^+$	3,3′-H	−2677	−2158	23
	4,4′-H	−3379	−2890	21
	5,5′-H	−2483	−2037	28
$Co^I(4,4'\text{-}(CH_3)_2bipy)_3^+$	3,3′-H	−2715	−2202	17
	4,4′-CH_3	+3080	+2928	21
	5,5′-H	−2429	−1990	23
$Co^I(bipy)_3^+$ [d] + air	3,3′-H	−4808	−4295	
	4,4′-H	...	...	
	5,5′-H	−2668	−2229	
$[Co^{II}(bipy)_3]Cl_2 \cdot H_2O$ [e]	3,3′-H	−4990	−4471	
	4,4′-H	−854	−365	
	5,5′-H	−2759	−2313	
$[Ni^{II}(bipy)_3]Cl_2 \cdot 2H_2O$ [f]	3,3′-H	−3620	−3151	
	4,4′-H	−852	−363	
	5,5′-H	−2740	−2294	
$[Ni^{II}(4,4'\text{-}(CH_3)_2bipy)_3]Cl_2 \cdot H_2O$ [f]	3,3′-H	−3613	−3100	
	4,4′-CH_3	+455	+607	
	5,5′-H	−2715	−2276	

[a] All the chemical shifts are relative to TMS, at 60 MHZ. [b] The contact shifts are calculated relative to the appropriate diamagnetic Fe(II) complex[2] at 28°. [c] $\Delta\nu_{1/2}$ is the line width at half-height. [d] 4,4′-Hydrogen signal is obscured by a solvent peak. [e] Data taken from ref 2. [f] Data taken from ref 3.

(7) R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969).
(8) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
(9) J. P. Jesson, *ibid.*, **47**, 579 (1967).
(10) D. R. Eaton in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968, pp 514–529.
(11) D. R. Eaton and W. D. Phillips in "Advances in Nuclear Magnetic Resonance," Vol. I, J. S. Waugh, Ed., Academic Press, New York, N. Y., 1965, pp 103–148.
(12) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).
(13) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).
(14) N. Maki, M. Yamagami, and H. Itatani, *J. Amer. Chem. Soc.*, **86**, 514 (1964).
(15) B. Martin and G. M. Waind, *J. Chem. Soc.*, 4284 (1958).

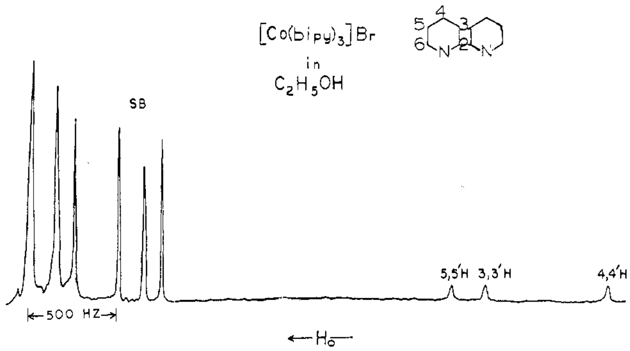

Figure 1.—Nmr spectrum of $[Co^{I}(bipy)_3]Br$ in C_2H_5OH at 301°K and numbering scheme used for bipyridine.

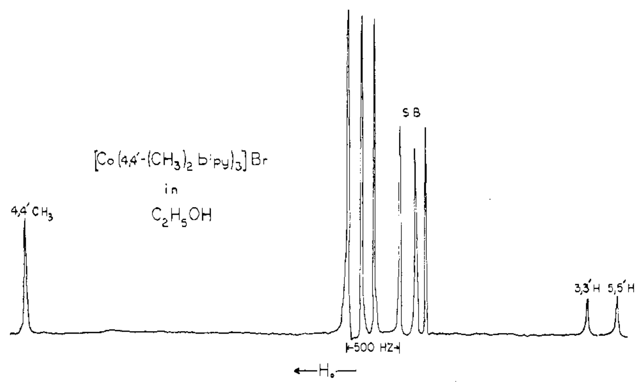

Figure 2.—Nmr spectrum of $[Co^{I}(4,4'\text{-}(CH_3)_2bipy)_3]Br$ in C_2H_5OH at 301°K.

relatively low solubility of the complexes has rendered these signals undetectable.

The nmr data for the substituted and unsubstituted tris (2,2′-bipyridine)cobalt(I) complexes, their oxidation products, and the analogous Ni(II) complexes are given in Table I.

Our uv data for the tris(2,2′-bipyridine)cobalt(II) -cobalt(I) complexes and 4,4′-dimethylbipyridine are given in Table II and are compared with previously reported values.[16,17]

TABLE II
UV SPECTRAL RESULTS

Compound	$\pi \rightarrow \pi^*$, nm		Ref
$Co^{II}(bipy)_3{}^{2+}$	305, 295		This work
$Co^{I}(bipy)_3{}^{+}$	. . .	285	This work
$Co^{II}(bipy)_3{}^{+}$	305, 295		17
$Co^{I}(bipy)_3{}^{+}$		284	16
$Co^{II}(4,4'\text{-}(CH_3)_2bipy)_3{}^{2+}$	303, 293		This work
$Co^{I}(4,4'\text{-}(CH_3)_2bipy)_3{}^{+}$	. . .	277	This work

Discussion

Evidence for the Presence of the Co(I) Complexes in Solution.—Gil, *et al.*,[16] have shown that the frequency of the $\pi \rightarrow \pi^*$ transition in the uv spectra of 2,2′-bipyridine–transition metal complexes is a function of the oxidation state of the metal. These $\pi \rightarrow \pi^*$ transitions commonly occur around 283 and 305 nm for the oxidation states I and II, respectively. Our data in Table II are in good agreement with previously reported results and clearly indicate that the Co(I) complexes are present in solution.

(16) L. Gil, E. Moraga, and S. Bunel, *Mol. Phys.*, **12**, 333 (1967).
(17) H. L. Schlafer, *Z. Phys. Chem.* (*Frankfurt am Main*), **8**, 373 (1956).

Also, the contact shift data for the air-oxidation product of $Co^{I}(bipy)_3{}^{+}$ are in good agreement with previously reported data[2] for $[Co^{II}(bipy)_3]Cl_2 \cdot H_2O$ (see Table I). When air was bubbled through the solution containing the Co(I) complex, the color turned from a dark blue to yellow almost immediately. The position of the proton resonances also shifted markedly, although the peak widths were not greatly altered, indicating a rapid electron exchange between the Co(I) species and the Co(II) species. This is in agreement with the previously reported[5] rapid electron transfer between the Fe(II) and Fe(III) chelates of *o*-phenanthroline but should be contrasted with the slow electron exchange reported by La Mar and Van Hecke[4] between the Cr(II) and Cr(III) complexes of *o*-phenanthroline and bipyridine.

Since the nmr data for the Co(I) complexes were reproducible over several runs, this indicates that our samples were not contaminated by appreciable amounts of the Co(II) complex. Also, the uv data indicate the purity of the Co(I) complexes.

Interpretation of the Contact Shift Data.—Before interpreting the observed contact shift data in terms of metal–ligand bonding and spin delocalization mechanisms, we must discuss possible pseudocontact shift contributions. Although the *g* tensor in these Co(I) compounds is unknown, we would expect that it is nearly isotropic, even under D_3 symmetry, as is the case for the isoelectronic Ni(II) complexes of D_3 symmetry.[18] In fact, several studies of Co(I) in an octahedral environment have shown isotropic *g*-tensor values.[19,20] We therefore assume pseudocontact contributions to be negligible and consider the observed shifts to be Fermi contact in origin.

A comparison of the contact shift data for the analogous, isoelectronic Co(I) and Ni(II) complexes (see Table I) shows that they differ principally in the large contact shifts at the 4,4′ positions observed in the Co(I) complexes. One would expect a σ-delocalization mechanism to be important in this compound since the unpaired electrons are located in the $\sigma_{2e}{}^*$ molecular orbital.[21] This would place positive spin density on the ligands and give rise to the observed downfield contact shifts. Although the contact shifts are all of the same sign, they do not show the expected attenuation characteristic of previously reported σ-type delocalization.[22,23] Also, substitution of a methyl group for a hydrogen at the 4,4′ positions leads to a contact shift of the opposite sign and approximately the same magnitude. This has been taken[24] as an indication of a π de-

(18) M. Peter, *Phys. Rev.*, **116**, 1432 (1959).
(19) W. Hayes and D. A. Jones, *Proc. Phys. Soc.*, **71**, 503 (1958).
(20) J. W. Orton, P. Auzins, and J. E. Wertz, *Phys. Rev.*, **119**, 1691 (1960).
(21) Under D_3 symmetry the $e\pi$ orbitals may mix with the $e\sigma$ orbitals, the metal t_{2g} orbitals are split into 1e and a_1 orbitals, and the metal e_g orbitals transform as 2e.
(22) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2523 (1968).
(23) D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967).
(24) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

localization of unpaired spin. Thus, we are compelled to conclude that some type of π-delocalization mechanism is operative in this system in addition to the previously discussed σ-delocalization mechanism. Recently, Cramer and Drago[25] have interpreted the contact shifts of octahedral Ni^{II}–py complexes in terms of a mixture of σ- and π-delocalization mechanisms. They also proposed that such mixed delocalization mechanisms may be quite common in other systems. We concur with their proposal and offer evidence to support it in these Co(I) complexes, *vide infra*.

There are several possible mechanisms for π delocalization and we shall attempt to choose between them on the basis of our experimental data and the published eigenvectors for 2,2′-bipyridine using both an extended Hückel method[3] and a McLachlan-type calculation.[4]

A direct back-bond from the metal 2e orbitals into the lowest unfilled π^* orbital ψ_7[26] would place positive spin density on the ligand and should result in a large downfield shift for the 4,4′-methyl groups and an upfield shift for the 4,4′-hydrogens—contrary to what is observed.

There may also be a direct overlap of the metal 2e orbitals, containing the unpaired spin, with the highest filled π orbital ψ_4. This mechanism would also transmit positive spin density from the metal onto the ligand. Both the extended Hückel calculations[3] and the McLachlan calculations[4] show a node in the wave function ψ_4 at the 4,4′-carbon atom. Further the McLachlan calculation[4] shows a sizable negative spin density at the 4,4′-carbon atom. This would lead to the observed downfield shift for the 4,4′-hydrogens and upfield shift for the 4,4′-methyl groups.

There is one other plausible mechanism that must be discussed. This would involve an exchange polarization of the paired a_1 and 1e metal electrons by the unpaired metal 2e electrons. Such a mechanism was discussed by Wicholas and Drago[3] for the Ni^{II}–bipy complexes. A similar mechanism has also been used recently to account for the π delocalization observed in Ni^{II}–py complexes.[25] This polarization would place net unpaired positive spin density on the metal leaving net unpaired negative spin density on the ligand. Thus, negative spin density could be placed in the empty π^* orbital ψ_7 which has the correct symmetry to overlap with the metal 1e orbitals. This mechanism would also lead to the observed downfield shift for the 4,4′-hydrogens and the upfield shift for the 4,4′-methyl groups. However, in the previously discussed cases, the observed contact shifts at the 4,4′ position were much smaller than those that we have observed in the cobalt(I)–bipyridine complexes. As Cramer and Drago[25] have pointed out, such a mechanism is likely to produce only a small amount of delocalization. Therefore, we conclude that a direct π delocalization involving transfer of positive spin density from the metal 2e orbitals to the highest filled π orbital is most likely to be the dominant π-delocalization mechanism in these Co^{I}–bipy complexes.

If one assumes the delocalization at the 4,4′-methyl position to be dominated by a π mechanism, then one may compare the relative extent of π bonding at this position for the Ni^{II}– and the Co^{I}–bipy complexes. The magnetic moment of a Co^{I}–bipy complex has been measured[27] and μ_{eff} = 2.89 BM. The magnetic moment of $[Ni(bipy)_3]Cl_2 \cdot 6H_2O$ has been reported as 2.88 BM.[28] The hyperfine coupling constants were calculated using eq 1 and assuming Curie law behavior. The results of these calculations are given in Table III.

TABLE III
A COMPARISON OF HYPERFINE COUPLING CONSTANTS AT THE 4,4′-CH_3 POSITION

Compound	$\Delta\nu_{4,4'-CH_3}$, Hz	g_{av}	$A_{4,4'-CH_3}$, G
$Co^{I}(4,4'-(CH_3)_2bipy)_3^+$	+3080	2.00	−0.249
$Ni^{II}(4,4'-(CH_3)_2bipy)_3^{2+}$	+455[a]	2.00	−0.052

[a] Data taken from ref 3.

Since previous studies[22,23] on delocalization in σ systems have shown that the 4,4′-methyl group is too far removed from the coordination site to be affected by σ delocalization, it is reasonable to infer that there is a substantial increase in the relative amount of π bonding at the 4,4′-methyl position in going from Ni(II) to Co(I). From the data in Table I it also appears likely there is a concomitant decrease in the relative amount of σ delocalization in going from Ni(II) to Co(I). The contact shifts for the 3,3′-hydrogens, which are most likely to be dominated by a σ delocalization,[3] are considerably smaller for the Co(I) complexes than for the Ni(II) complexes. However, without the contact shifts for the 6,6′-hydrogens, which are dominated by a σ-delocalization,[4] it is impossible to state unambiguously that this decrease in observed contact shifts does not arise from an increase in π delocalization at the 3,3′- and 5,5′-hydrogens which would produce the same effects. The increase in π bonding with decrease in positive charge for an isoelectronic series follows the well-known trend observed for metal carbonyl complexes.[29]

In conclusion, our data show that both σ- and π-delocalization mechanisms contribute to the observed contact shifts in these Co(I) complexes and that the dominant π-delocalization mechanism involves a direct overlap of the metal 2e orbitals with the highest filled π-symmetry ligand orbitals. Also, there is a substantial increase in the relative amount of π bonding in going from Ni(II) to Co(I) in these complexes.

Acknowledgment.—This work was supported by a U. S. Army research grant (DA-ARO-D-31-124-G1130) and a Petroleum Research Fund unrestricted grant (No. 3318-C-3,5).

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(26) The numbering of the ligand molecular orbitals follows the convention used by M. Wicholas and R. S. Drago, *ibid.*, **90**, 6946 (1968).

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(28) R. W. Asmussen in "Magneto Kemiske Undersogelser over Uorganiske Kompleksforbindsler," Gjellerups Forlang, Copenhagen, Denmark, 1944.
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