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Theoretical Study of Cis-Trans Isomerization in Simple Transition-Metal Complexes

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PRDDO calculations on several simple octahedral transition-metal complexes are presented. Relative energies, optimized geometries, and population analyses are discussed for a series of complexes of general formulas $M(NH_3)_4(CO)_2$ and $M(NH_3)_2(CO)_4$, M = Cr^0, Mn^+, Fe^{2+}, and Co^{3+}. Back-bonding stabilizes the cis isomers of the chromium and manganese complexes, but not those of Fe^{2+} or Co^{3+}. Similar calculations on $Cr(CO)_2(N_2)_4$ and $Cr(CO)_4(N_2)_2$ also predict the cis isomers to be favored energetically and are consistent with available experimental evidence. The cis isomers of $Cr(CO)_2(PH_3)_4$ and $Cr(CO)_4(PH_3)_2$ are both favored by less than 0.3 kcal/mol, even though the cis conformations of the corresponding amine complexes are strongly favored (6-13 kcal/mol). As reported previously, PH_3 can act as a π acceptor even without d orbitals on phosphorus, the acceptor orbital being best described as P-H σ^*. The energetic manifestation of this effect is a reduction of the cis-trans isomerization energy. Finally, calculations on the conformational preferences of bis(pyridine)bis(acetylacetonato)metal complexes are discussed.

Introduction

The phenomenon of π bonding in organometallic compounds has been studied intensely from both experimental and theoretical perspectives. Some of the most obvious and important consequences of π-bonding effects are in the areas of site preferences, conformational stability, and relative bond lengths. A good example of how π bonding can influence site preference may be found in Hoffmann's work on transition-metal pentacoordination, where the site preferences of π-bonding ligands are detailed for trigonal-bipyramidal and square-pyramidal structures.[1] Conformational preferences due to π bonding have been studied in a variety of systems.[2] Experimental studies of the effects of π bonding on bond lengths abound in the literature, but some of the clearest results are found in chromium-carbonyl complexes with phosphine,[3] where a distinct trend of long metal-ligand bond lengths trans to strong π acceptors can be seen. Here, we present a theoretical study of conformational preferences and relative bond lengths in an isoelectronic and isostructural series of complexes of chromium, manganese, iron, and cobalt.

Consider a (hypothetical) complex such as $Cr(NH_3)_4(CO)_2$. The pseudooctahedral coordination leads to the usual d-orbital splittings, with three occupied t_{2g} orbitals at low energy and two empty e_g orbitals at higher energy (here and throughout this paper we employ octahedral symmetry notation for simplicity). Simple π-bonding arguments lead one to predict that this complex should exist in the cis form, since only that conformation allows π back-bonding to the carbonyls from all three t_{2g} orbitals. Similar conclusions can be reached for systems such as $Cr(NH_3)_4(CO)_2$ although here all three t_{2g} orbitals are π bonding in both isomers. Nevertheless, the cis isomer reduces the number of mutually trans carbonyls and thus should be preferred. Indeed, in the absence of steric effects, mixed complexes of carbonyl and other non- or lesser-π-accepting ligands invariably assume the cis conformation. Examples are $Cr(CO)_2(PH_3)_4$,[3] $Cr(CO)_3(PH_3)_3$,[4] $Cr(CO)_4(PH_3)_2$,[5] and $Mo(CO)_4(PMe_3)_2$,[6] all of which exist in the cis form. ΔG for the cis-trans isomerization of the last compound is 0.32 kcal/mol, while more bulky phosphines are preferentially trans for steric reasons.[6]

The effects of π bonding on the bond lengths of these and similar complexes are also clear. Thus, in *cis*-$Cr(CO)_2(PH_3)_4$, the Cr-P distance trans to CO is 2.34 Å, while the corresponding distance trans to PH_3 is significantly shorter (2.28 Å).[3]

In this paper, we study the geometric and energetic consequences of π bonding in a group of octahedral complexes of general formulas $M(NH_3)_4(CO)_2$ and $M(NH_3)_2(CO)_4$, with M = Cr,^{0} Mn^+, Fe^{2+}, and Co^{3+}. We will show that π-back-bonding effects are important for Cr^0 and Mn^+, but not for Fe^{2+} or Co^{3+}. Calculations on the closely related system $Cr(CO)_{6-x}(N_2)_x$, which has recently been characterized spectroscopically,[7] are also discussed. We also present analogous calculations on the complexes $Cr(CO)_2(PH_3)_4$ and $Cr(CO)_4(PH_3)_2$. We show that there are significant differences between the isomerization energies of the amine and the phosphine complexes due to the π-accepting ability of PH_3 even without d orbitals on phosphorus. Finally, we present calculations on the complexes *trans*-bis(pyridine)bis(acetylacetonato)cobalt(II) and *trans*-bis(pyridine)bis(acetylacetonato)nickel(II), which have been studied previously with regard to the possible π-accepting ability of pyridine.[8,9] We show that π effects in these complexes are negligible.

Table I. Isomerization Energies[a]

compd	ΔE	compd	ΔE
$Cr(NH_3)_4(CO)_2$	−13.4	$Cr(NH_3)_2(CO)_4$	−6.3
$Mn(NH_3)_4(CO)_2{}^+$	−6.1	$Mn(NH_3)_2(CO)_4{}^+$	−1.5
$Fe(NH_3)_4(CO)_2{}^{2+}$	+1.0	$Fe(NH_3)_2(CO)_4{}^{2+}$	−0.1
$Co(NH_3)_4(CO)_2{}^{3+}$	+1.3	$Co(NH_3)_2(CO)_4{}^{3+}$	+1.0

[a] $\Delta E = E_{cis} - E_{trans}$, in kcal/mol.

Calculations

All calculations reported here were done within the PRDDO approximation,[10,11] with basis sets reported earlier.[12] The PRDDO method is an approximate but nonempirical approach that closely reproduces an ab initio calculation with the same basis set, while using substantially less computational time. The Slater orbital basis sets employed are minimal, with the important exception that the transition-metal d orbitals are represented by a fixed-contracted double-ζ set of Slater d orbitals obtained from exponent optimizations on the ground state of the atoms. The valence 4s and 4p exponents were taken to be 2.0. PRDDO has been shown[13] to predict excellent geometries in a wide variety of complexes of Cr, Mn, Fe, and Co, including $Cr(CO)_6$, $Cr(CO)_2(PH_3)_4$, and $Co(NH_3)_6{}^{3+}$, and thus would seem to be an appropriate method for this study, especially because extensive geometry optimizations will be required for a meaningful assessment of isomerization energies.

For the mixed amine-carbonyl complexes, all geometrical parameters were chain optimized except the N-H distance (held constant at 1.02 Å), the H-N-H angle (fixed at 109°), and the ligand-metal-ligand angles (set to 90°). The relative orientation of the amine ligands for the M-

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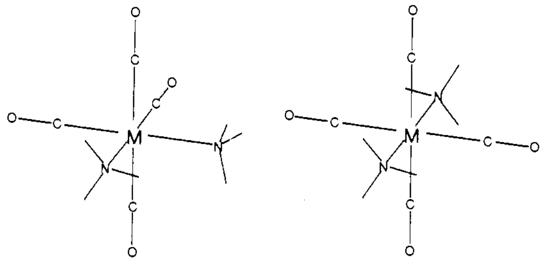

Figure 1. *cis*- and *trans*-$M(NH_3)_2(CO)_4$ complexes, showing the relative orientation of the ammonia ligands.

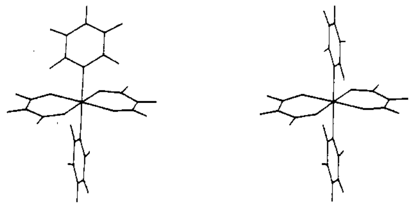

Figure 2. Staggered and eclipsed $M(acac)_2(py)_2$ complexes.

Table II. d_π-Orbital Populations of Carbonyl–Ammonia Complexes

complex	isomer	population	Δ
$Cr(NH_3)_4(CO)_2$	trans	4.89	0.09
	cis	4.80	
$Mn(NH_3)_4(CO)_2{}^+$	trans	5.45	0.06
	cis	5.39	
$Fe(NH_3)_4(CO)_2{}^{2+}$	trans	5.96	−0.01
	cis	5.97	
$Co(NH_3)_4(CO)_2{}^{3+}$	trans	5.99	0.00
	cis	5.99	
$Cr(NH_3)_2(CO)_4$	trans	4.60	0.04
	cis	4.56	
$Mn(NH_3)_2(CO)_4{}^+$	trans	5.27	−0.01
	cis	5.28	
$Fe(NH_3)_2(CO)_4{}^{2+}$	trans	5.94	0.00
	cis	5.94	
$Co(NH_3)_2(CO)_4{}^{3+}$	trans	5.98	0.00
	cis	5.98	

$(NH_3)_2(CO)_4$ complexes is shown in Figure 1 as a typical example. The estimated computational uncertainty for the optimized bond lengths is 0.005 Å. The carbonyl–phosphine complexes were optimized in a similar fashion, except that all unique ligand–metal–ligand angles were also optimized. The P–H distance was taken as 1.42 Å, while the H–P–H angle was set at 96.9°, the optimized value for both *cis*- and *trans*-$Cr(CO)_2(PH_3)_4$. The complexes $Cr(CO)_4(N_2)_2$ and $Cr(CO)_2(N_2)_4$ were fully optimized. Staggered and eclipsed *trans*-bis(pyridine)bis(acetylacetonato)cobalt(II) and the corresponding nickel complex (Figure 2) were constructed from the structural parameters in the literature.[8,9] All calculations were done within the closed-shell Hartree–Fock formalism, except for the last two, which were done by the unrestricted Hartree–Fock method, with three and two unpaired electrons, respectively.

Results and Discussion

We discuss the tetraammine–dicarbonyl complexes first, since these species exhibit the most pronounced π-bonding effects. The calculated isomerization energies are given in Table I. Both the chromium and manganese complexes exhibit a strong preference for the cis isomer, while the iron and cobalt species favor the trans isomer by about 1 kcal/mol. The d_π orbital populations (Table II) clearly indicate substantial back-bonding for chromium and manganese, but not for iron or cobalt, where essentially no depopulation of the d_π orbitals is seen. The greater depopulation of the d_π orbitals in the cis isomers of the Cr and Mn compounds is a clear indication of greater back-bonding in this isomer. The small preference for the trans arrangement in the Fe and Co complexes is probably due to steric effects between the ammonia ligands, which are slightly more pronounced in the cis isomers. The optimized geometries (Table III) clearly show the effects of π bonding. While the optimized metal–ammonia bond lengths decrease monotonically from Cr^0 to Co^{3+}, the metal–carbonyl distances vary as Cr ≈ Mn < Fe ≈ Co, with the short distances for chromium and manganese clearly due to back-bonding. The average metal–carbonyl distances in the chromium and manganese complexes (1.87 and 1.88 Å, respectively) compare well with similar experimental distances of 1.82 Å in *cis*-$Cr(CO)_2(PH_3)_4$[3] and 1.85–1.89 Å in $Mn(CO)_5H$[14] and $Mn(CO)_5Cl$.[15] The optimized C–O distances are significantly longer in the Cr and Mn complexes. This is expected, since metal–ligand back-bonding will populate the CO π* orbital and decrease the C–O bond order. To our knowledge, none of the dicarbonyl species discussed here are known experimentally. $Cr(NH_3)_3(CO)_3$ has been synthesized[16] but apparently not characterized structurally. Finally, metal–carbonyl overlap populations (Table IV) indicate slightly stronger overlap in the cis isomers for all the complexes, with the effect

Table III. $M(NH_3)_4(CO)_2$ Geometries[a]

metal	isomer	M–C	M–N	M–N[b]	CO
Cr	trans	1.879	2.174	...	1.177
	cis	1.858	2.172	2.171	1.179
Mn	trans	1.890	2.093	...	1.154
	cis	1.868	2.089	2.087	1.153
Fe	trans	2.081	2.030	...	1.141
	cis	2.083	2.027	2.034	1.141
Co	trans	2.080	1.950	...	1.141
	cis	2.064	1.945	1.958	1.141

[a] All distances in A. [b] Trans to N.

Table IV. $M(NH_3)_4(CO)_2$ Metal–Ligand Overlap Populations

metal	isomer	M–C	M–N	M–N[a]
Cr	trans	0.293	0.150	0.154
	cis	0.316	0.147	0.154
Mn	trans	0.123	0.158	...
	cis	0.130	0.157	0.162
Fe	trans	0.162	0.225	...
	cis	0.166	0.221	0.225
Co	trans	0.247	0.310	...
	cis	0.249	0.307	0.309

[a] Trans to N.

Table V. $M(NH_3)_2(CO)_4$ Geometries[a]

metal	isomer	M–C	M–C[b]	M–N	C–O	
Cr	trans	1.907	...	2.148	1.161	...
	cis	1.900	1.881	2.147	1.160	1.162[b]
Mn	trans	1.914	...	2.072	1.148	...
	cis	1.917	1.905	2.069	1.147	1.148[b]
Fe	trans	2.082	...	2.021	1.140	...
	cis	2.077	2.083	2.016	1.140	1.140[b]
Co	trans	2.024	...	1.949	1.141	...
	cis	2.057	2.029	1.941	1.141	1.141[b]

[a] All distances in A. [b] Trans to N.

Table VI. $M(NH_3)_2(CO)_4$ Metal–Ligand Overlap Populations

metal	isomer	M–C	M–C[a]	M–N
Cr	trans	0.247	...	0.184
	cis	0.248	0.268	0.180
Mn	trans	0.132	...	0.186
	cis	0.131	0.133	0.182
Fe	trans	0.187	...	0.248
	cis	0.187	0.190	0.243
Co	trans	0.278	...	0.325
	cis	0.285	0.278	0.326

[a] Trans to N.

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Table VII. Optimized Geometries for $Cr(CO)_2(N_2)_4$ and $Cr(CO)_4(N_2)_2$ Complexes[a]

complex	Cr-C		Cr-N		C-O	N-N
trans-$Cr(CO)_2(N_2)_4$	1.937		1.941		1.154	1.139
cis-$Cr(CO)_2(N_2)_4$	1.920		1.942[b]	1.950	1.156	1.139[c]
trans-$Cr(CO)_4(N_2)_2$	1.918		1.941		1.154	1.139
cis-$Cr(CO)_4(N_2)_2$	1.914[b]	1.925	1.948		1.155[c]	1.139

[a] All distances are in Å; all ligand-metal-ligand angles are 90 ± 2.5°. [b] Trans to N. [c] The optimized values are identical for both chemically distinct positions.

Table VIII. $Cr(CO)_2(PH_3)_4$ Geometries[a]

	Cr-C		Cr-P		Cr-P[b]		
isomer	calcd	exptl	calcd	exptl	calcd	exptl	C-O
trans	1.875		2.307				1.171
cis	1.861	1.817	2.329	2.338	2.305	2.282	1.172

[a] All distances are in Å. All optimized ligand-metal-ligand angles are 90 ± 3°. [b] Trans to P.

Table IX. $Cr(CO)_4(PH_3)_2$ Geometries[a]

	Cr-C		Cr-C[b]		Cr-P		
isomer	calcd	exptl	calcd	exptl	calcd	exptl	C-O
trans	1.984				2.275		1.161
cis	1.888	1.839	1.880	1.836	2.315	2.346	1.162

[a] All distances are in Å. All optimized ligand-metal-ligand angles are 90 ± 3°. [b] Trans to P.

being most pronounced for Cr and Mn. Further analysis of these overlap populations shows that a large component of the metal-carbonyl overlap in $Cr(NH_3)_4(CO)_2$ and $Mn(NH_3)_4(CO)_2^+$ is due to π bonding, while the iron and cobalt complexes show essentially pure σ overlap.

Analogous results for the tetracarbonyl complexes are given in Tables I, II, V, and VI. In general similar effects are seen, except that the differences between the energies, bond lengths, orbital populations, etc. of the cis and trans isomers are reduced considerably, due to the fact that both isomers now have three π-bonding d orbitals. The tetracarbonyl species are again not known experimentally; however, mixed carbonyl-dinitrogen complexes of chromium have recently been characterized spectroscopically in liquid xenon at 183 K. Our optimized geometries for $Cr(CO)_2(N_2)_4$ and $Cr(CO)_4(N_2)_2$ are given in Table VII, and the d_π-orbital populations are presented in Table VIII. Dinitrogen is a significantly weaker π acceptor than CO. PRDDO calculations on $Cr(CO)_6$ and $Cr(N_2)_6$ show d_π-orbital populations of 4.45e and 4.79e, respectively (the eigenvalue of the LUMO in isolated N_2 is actually slightly lower than that of CO, but the CO LUMO is highly polar toward C, making it a better acceptor orbital than the nonpolar LUMO in N_2). PRDDO calculations predict the cis isomer of $Cr(CO)_2(N_2)_4$ to be 2.2 kcal/mol more stable than the trans arrangement, which is apparently not observed experimentally. Similarly, we calculate *cis*-$Cr(CO)_4(N_2)_2$ to be favored by 1.6 kcal/mol; however, the relative abundance of the two isomers is not known experimentally.[7]

Mixed carbonyl-phosphine complexes of chromium behave very differently from those of NH_3. Optimized geometries (Tables VIII and IX) generally show less variation between the cis and trans isomers, and the d_π-orbital populations are essentially constant (4.74e for $Cr(CO)_2(PH_3)_4$ and 4.50e for $Cr(CO)_4(PH_3)_2$). The isomerization energies drop dramatically to 0.3 and 0.04 kcal/mol, respectively. We have previously shown[17] that this effect is due to the fact that PH_3 acts as a π acceptor even though no d orbitals are included in the phosphorus basis set. The π-accepting orbitals are best described as P-H σ^*'s. We have confirmed the π-accepting ability of PH_3 via σ^* orbitals for a model complex at the ab initio level with a double ζ basis set with and without d orbitals on phosphorus, where the addition of d orbitals on phosphorus does little if anything to enhance the π-accepting ability of PH_3.[17] The energetic manifestation of this effect is the reduction of the isomerization energies, due to the greater stabilization of the t_{2g} orbitals in *both* isomers. We have not calculated isomerization energies for mixed carbonyl-phosphine complexes of Mn^+, Fe^{2+}, and Co^{3+}, since the obvious extrapolation from the results presented here leads to the prediction of no important π-bonding effects, with perhaps a slight favoring of the trans isomers due to steric effects.

Finally, we briefly mention the conformational preferences of the complexes *trans*-bis(pyridine)bis(acetylacetonato)cobalt(II) and -nickel(II). Experimentally, the cobalt complex is known to exist in the staggered configuration.[8] While this was initially interpreted as evidence for metal-pyridine π bonding, the corresponding nickel complex was subsequently determined to be eclipsed.[9] Thus, the experimental conformation is probably related more to crystal-packing forces than π-bonding effects.[9] This is fully consistent with our cis-trans isomerization energy results, which show no π-bonding effects when the formal charge on the metal is larger than 1+. PRDDO calculations on these two complexes predict the eclipsed arrangement to be favored by 3.6 kcal/mol (Co) and 2.9 kcal/mol (Ni). No significant depopulation of the metal d_π orbitals is observed. The stability of the eclipsed conformations would appear to be due to intramolecular steric effects and not any important electronic interactions. This is evident from calculations on the eclipsed conformations with the pyridine rings over the acac ligands, rather than between them as shown in Figure 2. These eclipsed conformations are 6.2 kcal/mol (Co) and 8.2 kcal/mol (Ni) less stable than the eclipsed structure in Figure 2. Crystal-packing forces, which are, of course not included in our calculations, have been estimated to favor the staggered conformations slightly in both complexes.[9]

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Registry No. $Cr(NH_3)_4(CO)_2$, 94904-57-1; $Mn(NH_3)_4(CO)_2^+$, 94904-58-2; $Fe(NH_3)_4(CO)_2^{2+}$, 94904-59-3; $Co(NH_3)_4(CO)_2^{3+}$, 94904-60-6.

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