Density Functional Study of Spin State in CpM(NO)X$_2$ (M = Mo, Cr; X = Cl, NH$_2$, CH$_3$): Spectrochemical and Nephelauxetic Effects in Organometallic Compounds[1]

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The relationship between spin state and metal−ligand bonding interactions in CpM(NO)-X$_2$ species was investigated using density functional computational techniques. The geometries of CpM(NO)Cl$_2$ (M = Cr, Mo), CpCr(NO)(NH$_2$)X, and CpCr(NO)(CH$_3$)X (X = Cl, CH$_3$) were optimized at the DFT-B3LYP level for both the diamagnetic ($S = 0$) and paramagnetic ($S = 1$) electronic configurations. While the geometric parameters of the singlet compounds matched well with structures determined experimentally, the Cr−NO bond lengths in the triplet species exceeded the experimentally observed range by a significant margin, thereby indicating a propensity for nitrosyl-ligand dissociation from the high-spin complexes. The order of relative singlet vs triplet spin-state stability (expressed as ΔE_{s-t} (kcal/mol)) was determined to be CpCr(NO)Cl$_2$ (8.20) > CpCr(NO)(CH$_3$)Cl (1.52) ≈ CpCr-(NO)(NH$_2$)Cl (0.95) > CpCr(NO)(CH$_3$)$_2$ (−2.37) > CpCr(NO)(NH$_2$)CH$_3$ (−9.55) > CpMo(NO)-Cl$_2$ (−17.62). The amide π-donation increases the HOMO−LUMO energy splitting, thus favoring the diamagnetic configuration. The alkyl ligand reduces the electron−electron repulsion through orbital expansion, thereby lowering the relative energy of the singlet state. Extended Hückel molecular-orbital calculations were performed on the DFT-optimized structures to help rationalize the metal−ligand bonding interactions, and interelectron repulsions were quantified by evaluation of the Coulomb (J) and exchange (K) integrals based on the B3LYP-optimized triplet spin-state geometries.

Introduction

Much of the distinctive character of transition-metal chemistry is derived from the variable energies, occupancies, and bonding interactions of the d orbitals. Evaluating the effect of ligands on these electronic properties and the resulting ground and excited spin states of a complex has long been a fascinating and challenging area of study. Over the course of decades, developments in various spectroscopic and theoretical techniques have determined both the types of compounds which may be examined in this manner and the nature of the questions which may be investigated. Despite these changes, the two most important fundamental properties that determine the relative spin-state stabilities in transition-metal species have always been the *frontier-orbital splitting* energy and the *interelectron-repulsion* energy. Because these underlying principles remain constant, the intuitive concepts originally developed to describe and explain how ligands influence these parameters may be successfully applied to more sophisticated problems of current interest.

Early work in this area was conducted on pseudo-octahedral Werner-type coordination compounds. Magnetic susceptibility measurements allowed the ground spin state of these species to be determined, and UV/visible spectroscopy provided information about excited electronic configurations. The predominantly ionic bonding present in these compounds encourages the formation of mid-valent compounds with accessible high-spin configurations. The orbitals are essentially metal-centered, allowing electronic transitions to be readily assigned, as well as rendering the complexes amenable to theoretical treatment using relatively simple crystal field or ligand field descriptions. The systematic investigation of a large number of compounds demonstrated the effects of ligands on the splitting energy between the t$_{2g}$ and e$_g$ orbitals, Δ_0, and the interelectron-repulsion energy, represented by the Racah parameters, B and C.[2] Common ligands were ranked in the spectrochemical and nephelauxetic series, which reflected their empirically determined effects on Δ_0 and on the Racah parameters, respectively.

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In contrast, application of the concepts of orbital-splitting and spin-pairing energies to organometallic transition-metal complexes has generally been neglected. This is in part due to the covalent bonding and π-acceptor ligands typical of organometallic compounds, which tend to enforce a low-valent, diamagnetic configuration. The increased ligand character of the frontier orbitals hampers the assignment of the electronic transitions of the UV/vis spectra and limits the applicability of simple ligand field theory. Thus, magnetic susceptibility and UV/vis were supplanted by IR and NMR spectroscopy as the primary analytical tools for organometallic complexes, with subsequent investigations proceeding down avenues of inquiry suitable to the latter techniques.[3]

Recent improvements in X-ray crystallography and theoretical methods have contributed to the current reevaluation of the relevance of spin state to organometallic chemistry. The dramatic increase in well-characterized high-spin organometallic species[4] can be attributed in part to the increased application of X-ray crystallography as a characterization technique[5] and the attendant shift away from the diamagnetic bias inherent in NMR spectroscopy. Open-shell compounds have demonstrated their utility in olefin polymerization[6] and dinitrogen cleavage[7] reactions. While accurate evaluation of energetically similar electronic states has long been a formidable challenge, advances in *ab initio*[8] and hybrid density functional[9] computational techniques have helped theoretical chemists address these near-degeneracy problems.[10] With the application of theoretical methods to the examination of unsaturated organometallic species too transient or unstable to be observed experimentally,[11] it is becoming increasingly apparent that the relative energies of the spin states of these intermediates constitute a critical but previously unappreciated factor in several important reactions.[12] For example, calculations indicate that a low-lying

triplet *excited* state assists the intermolecular C−H bond activation reactions exhibited by CpM(CO) (M = Rh, Ir) and related complexes, yet because CpCo(CO) possesses a triplet *ground* spin state, it neither binds nor activates alkanes.[13]

Recent investigations of $CpM(NO)X_2$ ($Cp = \eta^5\text{-}C_5H_5$; M = Cr, Mo; X = halide, alkyl, amide) species suggest that spin state plays a critical role in the stability of transition-metal nitrosyl complexes. $CpMo(NO)X_2$ compounds are derived from treatment of $CpMo(NO)(CO)_2$ with I_2[14,15] or PCl_5[16] and subsequent metathesis reactions of the dihalide species.[17] The 16e diamagnetic $CpMo(NO)(alkyl)_2$ species are of particular interest due to their unusual bonding,[18a] synthesis,[18b] thermolytic decomposition,[18c] and subsequent derivatization.[18d] In contrast, no $CpCr(NO)X_2$ compounds are isolable from analogous halogenation reactions of $CpCr(NO)(CO)_2$.[19] Chemical or electrochemical oxidation of $[NEt_4][CpCr(NO)Cl_2]$ instead results in the isolation of products consistent with the loss of NO from the initially formed neutral $CpCr(NO)Cl_2$ intermediate.[20] Complexes such as $CpCr(NO)(NPh_2)I$[21] and $CpCr(NO)(N^iPr_2)(CH_2SiMe_3)$,[22] however, have been demonstrated to be stable.

We have previously proposed that these observations are best accounted for by spin-state considerations. Unlike the stable, diamagnetic $CpMo(NO)X_2$ species, $CpCr(NO)Cl_2$ might adopt a high-spin, triplet configuration. If this configuration involves either the population of M−NO π-antibonding orbitals or the removal of electrons from M−NO π-bonding orbitals, the resultant weakening of the metal−nitrosyl bond may render the complex prone to NO dissociation.[20] The strong Cr−N(amide) π-bonding interaction observed for diamagnetic $CpCr(NO)(NR_2)X$ species may prevent this mode of decomposition by stabilizing the singlet state with respect to the triplet.[22]

This paper describes the results of a density functional study undertaken in order to address the following four questions. (1) What is the source of the discontinuity in $CpM(NO)X_2$ chemistry between Mo and Cr? (2) Does $CpCr(NO)Cl_2$ have an accessible high-spin state? (3) Does adopting an $S = 1$ configuration labilize the nitrosyl ligand? (4) How does varying the X ligands affect the relative energies of the singlet and triplet spin

(3) For example, the availability of NMR and IR spectroscopy permitted the investigation of fluxional organometallic species. For a retrospective account of this research, see: Cotton, F. A. *Inorg. Chim. Acta* **1997**, *256*, 177 and references contained therein.

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states? The geometries of six model compounds of the formula CpM(NO)X$_2$ (M = Cr, Mo; X = Cl, NH$_2$, CH$_3$) were optimized at the B3LYP level in both singlet and triplet electronic configurations, and the overall energies of the two spin states were compared. The gradient-corrected density functional (B3LYP) computational approach has been used in dynamic studies of important transition-metal-mediated reactions such as intermolecular alkane C−H bond activation,[13bc,23] dinitrogen bond cleavage,[7b] and olefin polymerization[6h,24] and has generally provided accurate geometries and energies.[24] Recent comparative studies have shown the B3LYP method to be remarkably effective in dealing with spin-state problems[25] and first-row transition metals,[10,23b] including first-row CpM(NO)-containing species.[26] We are therefore confident that the computational approach chosen here is providing us with meaningful results, especially in terms of trends. The calculations indicate that the ligand effects on the orbital-splitting and spin-pairing energies are critically important and that the familiar concepts developed to treat these parameters for classic coordination compounds translate remarkably smoothly to open-shell organometallic species. The theoretical determination of the combinations of alkyl, halide, and amide ligands which stabilize diamagnetic CpCr(NO)X$_2$ species will thus guide our future synthetic strategies.

Computational Details

All the calculations were performed using GAUSSIAN 94[27] on the DEC/Alphastation 250 at the University of Maryland in College Park and on the SGI Power Challenge at the Université de Bourgogne. The LanL2DZ set was employed to perform complete geometry optimization with a Density Functional Theory (DFT) approach. The three-parameter form of the Becke, Lee, Yang, and Parr functional (B3LYP)[28] was employed. The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H and C[29] and the relativistic electron core potential (ECP) sets of Hay and Wadt for the heavy atoms.[30] Electrons outside the core were all those of H, C, N, and O atoms, the 3s and 3p electrons in Cl, and the ns, np, nd, and $(n + 1)$s electrons in Cr ($n = 3$) and Mo ($n = 4$).

A C_s symmetry arrangement was imposed for the CpM(NO)Cl$_2$ and CpCr(NO)(CH$_3$)$_2$ systems. For these systems, only the

Cp configuration with the unique C−H group opposite to the NO ligand was considered. A recent theoretical study of CpMCl$_2$(PH$_3$) (M = Cr, Mo) has shown that the relative configuration of the Cp ligand does not significantly affect the total energy of the system.[25] No constraints were imposed for the C_1-symmetric systems. The starting geometries were constructed by adapting bond distances and angles from available X-ray structures. For singlet CpCr(NO)(NH$_2$)Cl, the optimization was carried out by starting from two different geometries, i.e., with the CrNH$_2$ moiety either coplanar or orthogonal with the N−Cr−NO plane; both converged to the same energy and geometry.

The mean value of the spin of the first-order electronic wave function, which is not an exact eigenstate of S^2 for unrestricted calculations on open-shell systems, was considered suitable for the unambiguous identification of the spin state. Spin contamination was carefully monitored, and the energies shown in the Results and Discussion correspond to unrestricted B3LYP (UB3LYP) calculations. The value of $\langle S^2 \rangle$ for the UB3LYP calculations on the spin triplet system at convergence was 2.0189 for CpMo(NO)Cl$_2$, 2.775 for CpCr(NO)Cl$_2$, 2.8242 for CpCr(NO)(NH$_2$)Cl, 2.6597 for CpCr(NO)(NH$_2$)(CH$_3$), 2.6723 for CpCr(NO)(CH$_3$)Cl, and 2.6840 for CpCr(NO)(CH$_3$)$_2$, indicating a slight spin contamination (greater for Cr than for Mo) which derives from mixing of states with higher spin.

The visualization of the orbital interactions and the orbital energy diagrams was assisted by extended Hückel molecular-orbital calculations, which were performed on the B3LYP-optimized geometries using the commercially available HyperChem for Windows Release 3 and ChemPlus extensions for Hyperchem.[20,31] An unweighted Hückel constant of 1.75 was used.

A monoelectronic HF analysis of the CpM(NO)X$_2$ complexes was performed according to the method developed by Simpson, Hall, and Guest.[32] The calculation of the relevant Coulomb (J) and exchange (K) integrals was based on the results of the B3LYP calculations of the triplet states. Excess spin natural orbitals (φ_1^α and φ_2^α with energies ϵ_1 and ϵ_2) were extracted by diagonalizing $S^{1/2}P^{\alpha-\beta}S^{1/2}$, where S is the overlap matrix and $P^{\alpha-\beta}$ is the excess spin density matrix, as detailed in a previous contribution.[25] The values of the Coulomb integrals J_{11} and J_{12} and the exchange integral K_{12} were obtained from these orbitals.

Results and Discussion

The model compounds CpM(NO)Cl$_2$ (M = Cr, Mo), CpCr(NO)(NH$_2$)X, and CpCr(NO)(CH$_3$)X (X = Cl, CH$_3$) were each geometry-optimized in both $S = 0$ and $S = 1$ electronic configurations. The geometry parameters are collected in Tables 1−3. By comparison of the overall energies, the relative stability of singlet vs triplet states was determined. All the optimized geometries were then examined at the extended Hückel molecular-orbital level of theory, and the Coulomb (J) and exchange (K) integrals were evaluated according to the method of Hall et al.,[32] as described in Computational Details.

Comparison of CpM(NO)Cl$_2$ (M = Cr, Mo). As shown in Figure 1, singlet CpMo(NO)Cl$_2$ is calculated to be considerably lower in energy than the triplet state. This is in agreement with experimental observations, since no triplet CpMo(NO)X$_2$ complexes are known,[17,18] in contrast to high-spin Mo(II) complexes such as Cp*Mo(PMe$_3$)$_2$Cl.[12] Although high-spin CpCr(NO)X$_2$

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Table 1. DFT-B3LYP-Optimized Geometries and Energies for CpM(NO)Cl₂ (M = Mo, Cr)

structural param[a]	CpMo(NO)Cl₂		CpCr(NO)Cl₂	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$
CNT−M	2.123	2.101	1.957	1.969
M−C(av)	2.449	2.432	2.305	2.318
M−Cl	2.395	2.405	2.272	2.296
M−NO	1.777	1.830	1.655	1.860
N−O	1.220	1.225	1.199	1.193
CNT−M−Cl	112.70	119.93	114.96	121.38
CNT−M−NO	123.10	112.11	126.42	119.22
Cl−M−Cl	114.95	94.62	108.36	98.14
Cl−M−NO	95.90	103.74	94.34	95.32
M−N−O	173.39	169.77	177.18	177.50
E (hartrees)	−420.9587	−420.9306	−439.6831	−439.6961

[a] CNT = Cp ring centroid.

Table 2. DFT-B3LYP-Optimized Geometries and Energies for CpCr(NO)(NH₂)X (X = Cl, CH₃)

structural param[a]	CpCr(NO)(NH₂)Cl[b]		CpCr(NO)(NH₂)(CH₃)[c]	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$
CNT−Cr	1.978	1.978	1.984	2.024
Cr−C(av)	2.324	2.391	2.329	2.364
Cr−X	2.330	2.329	2.071	2.057
Cr−NO	1.648	1.811	1.641	1.773
Cr−NH₂	1.796	1.927	1.803	1.924
N−O	1.210	1.210	1.224	1.216
CNT−Cr−X	113.01	119.53	111.66	117.60
CNT−Cr−NO	126.26	126.57	127.61	127.37
CNT−Cr−NH₂	118.36	125.69	121.26	125.65
X−Cr−NO	93.43	99.77	89.86	96.69
X−Cr−NH₂	104.22	92.81	100.70	91.87
ON−Cr−NH₂	97.09	82.86	98.85	88.65
Cr−N−O	175.94	174.80	175.85	175.97
ΣCrNH₂	360.00	358.55	359.93	358.50
H−N−Cr−N	11.39, −169.36	−74.37, 91.00	7.52, −169.11	−76.66, 88.35
E (hartrees)	−480.6751	−480.6766	−505.5853	−505.5701

[a] CNT = Cp ring centroid. [b] X = Cl. [c] X = CH₃.

Table 3. DFT-B3LYP-Optimized Geometries and Energies for CpCr(NO)(CH₃)X (X = Cl, CH₃)

structural param[a]	CpCr(NO)(CH₃)Cl[b]		CpCr(NO)(CH₃)₂[c]	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$
CNT−Cr	1.959	2.004	1.983	2.026
Cr−C(av)	2.307	2.347	2.328	2.365
Cr−CH₃	2.057	2.049	2.029	2.073
Cr−Cl	2.254	2.298		
Cr−NO	1.647	1.825	1.640	1.792
N−O	1.212	1.201	1.223	1.215
CNT−Cr−NO	126.04	121.95	127.77	137.38
CNT−Cr−CH₃	110.78	117.89	114.40	117.36
CNT−Cr−Cl	120.06	124.82		
X−Cr−CH₃	105.07	94.44	110.92	95.69
ON−Cr−Cl	100.41	94.12		
ON−Cr−CH₃	88.85	96.78	93.09	90.61
Cr−N−O	175.30	174.45	175.99	176.91
E (hartrees)	−464.5993	−464.6017	−489.4986	−489.4948

[a] CNT = Cp ring centroid. [b] X = Cl. [c] X = CH₃.

Figure 1. Relative energies and DFT-B3LYP-optimized geometries of ¹A′ and ³A′ CpM(NO)Cl₂ (M = Mo, Cr).

(NO)Cl₂ species is consistent with established periodic trends, since first-row transition-metal complexes are much more likely to adopt an open-shell configuration than their second- or third-row congeners.[4]

The M−NO bond length is the only structural parameter which changes dramatically between the high- and low-spin configurations in both CpM(NO)Cl₂ complexes. For Mo, this difference is relatively subtle, with the Mo−NO bond being 0.053 Å longer in the triplet state than in the singlet. In the Cr complex, however, the change is more dramatic, from 1.655 Å in the singlet to 1.860 Å in the triplet. The significance of this lengthening is underscored by the constancy of experimentally determined Cr−NO bond lengths, which fall in the narrow range of 1.65−1.69 Å for CpCr mononitrosyl complexes with a variety of ancillary ligands, overall charges, and formal oxidation states.[20−22,31,33] We interpret this 0.2 Å difference as signaling a critical weakening of the Cr−NO bond in the triplet configuration, consistent with the nitrosyl lability we proposed for high-spin CpCr(NO)Cl₂.[20]

Comparison of CpCr(NO)(NH₂)X (X = Cl, CH₃). The instability of CpCr(NO)Cl₂ with respect to NO loss effectively precludes its use as a precursor to other CpCr(NO)X₂ species by metathesis routes analogous to those used for the congeneric Mo compounds.[17,18] CpCr(NO)(NPh₂)I has previously been synthesized in unreported yield from the reaction of CpCr(NO)₂Cl and LiNPh₂ in the presence of MeI.[21] CpCr(NO)(NⁱPr₂)(η¹-O₂CPh) and CpCr(NO)(NⁱPr₂)(CH₂SiMe₃) were recently synthesized from Cr(NO)(NⁱPr₂)₃.[22] The solid-state molecular structures of all three CpCr(NO)(NR₂)X complexes display short Cr−N(amide) distances of 1.83−1.89 Å and planar Cr−NR₂ groups aligned with the Cr−NO axis, thereby suggesting a strong Cr−N(amide) π-interaction. Consequently, we examined the model

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complexes have never been observed directly, we recently proposed that the triplet spin state should at least be accessible for CpCr(NO)Cl₂.[20] Gratifyingly, the calculations afford a triplet ground state 8.20 kcal/mol lower in energy than the diamagnetic singlet state. The metal dependence of the ground spin state for CpM-
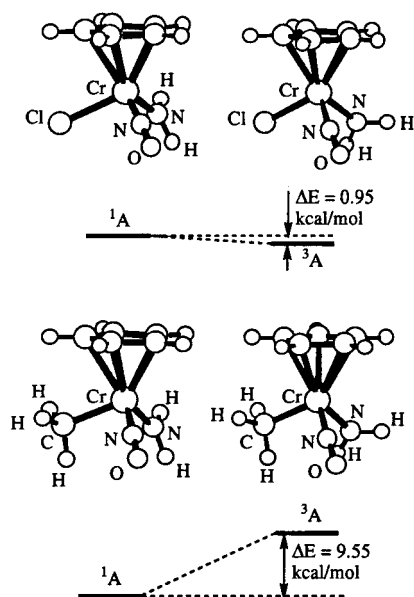
Figure 2. Relative energies and DFT-B3LYP-optimized geometries of ^1A and ^3A CpCr(NO)(NH$_2$)X (X = Cl, CH$_3$).

CpCr(NO)(NH$_2$)Cl to gauge the role of the Cr−N(amide) π-bond in conferring a low-spin configuration on these CpCr(NO)(NR$_2$)X species.

The optimized geometry of singlet CpCr(NO)(NH$_2$)-Cl, shown in Figure 2, conforms with the known molecular structures of CpCr(NO)(NR$_2$)X compounds. The amide ligand is planar, with the sum of the angles around N being 360°. The Cr−NH$_2$ bond length of 1.796 Å is slightly shorter than those determined experimentally, perhaps due to steric interaction between the Cp ring and the bulky NR$_2$ (R = Ph or ^{i}Pr) ligands of the amide complexes. The alignment of the amide along the Cr−NO axis indicated by the H−N−Cr−N torsion angles is consistent with the experimental results.[21,22]

The optimized geometry for triplet CpCr(NO)(NH$_2$)-Cl is remarkably different from that of the singlet state. As in triplet CpCr(NO)Cl$_2$, the Cr−NO distance has extended beyond the range observed experimentally. The Cr−amide distance has also lengthened and while the Cr−NH$_2$ group remains essentially planar, the ligand has adopted a conformation roughly perpendicular to the Cr−NO axis.

Comparison of the total energies of singlet and triplet CpCr(NO)(NH$_2$)Cl shows that the two configurations are nearly degenerate. Although the replacement of Cl$^-$ in CpCr(NO)Cl$_2$ with NH$_2^-$ has increased the relative stability of the singlet vs the triplet spin state, the calculation still favors the triplet state by 0.95 kcal/mol. The known CpCr(NO)(N^{i}Pr$_2$)X complexes (X = η^1-O$_2$-CPh, CH$_2$SiMe$_3$), on the other hand, are diamagnetic. Both compounds possess planar ON−Cr−NC$_2$ moieties in the solid state (X-ray crystallography), and the presence of four inequivalent amide CH$_3$ groups in the ^{1}H NMR spectra (room temperature, C$_6$D$_6$) suggests that this orientation is retained in solution. While $S = 1$ complexes of the formula CpCr(NR$_2$)L$_2$ are known,[34] the long Cr−NO bond (1.811 Å) in triplet CpCr(NO)-(NH$_2$)Cl suggests that adopting a high-spin configura-

tion would render CpCr(NO)(NR$_2$)X species prone to decomposition via NO loss.

The discrepancy between experimental observations and theoretical results could be due to the differences between the actual compounds and the simplified complex we have chosen as a model. For instance, the presence of electron-donating alkyl substituents makes N^{i}Pr$_2^-$ a better π-donor than the NH$_2^-$ ligand used in the model compound. Increased π-donation could enhance the stability of singlet CpCr(NO)(N^{i}Pr$_2$)X complexes to a greater extent than the calculations indicate. In addition, the filled p orbitals of the Cl$^-$ ligand may interfere with the Cr−NH$_2$ π-bonding interaction.[35,36]

To more closely approximate the known CpCr(NO)(N^i-Pr$_2$)(CH$_2$SiMe$_3$) complex, the model compound CpCr-(NO)(NH$_2$)(CH$_3$) was also examined. The geometry optimization for the methyl derivative, in either spin state, was slower relative to the chloride systems due to a shallow energy surface along the Cr−C bond rotation parameter but eventually converged to final geometries that closely match those determined for CpCr(NO)(NH$_2$)Cl (Table 1). The calculated singlet geometry closely corresponds to the experimentally determined geometry for CpCr(NO)(N^{i}Pr$_2$)(CH$_2$SiMe$_3$).[22] Singlet CpCr(NO)(NH$_2$)(CH$_3$) was calculated to be 9.55 kcal/mol *more stable* than the triplet state, as indicated in Figure 2.

The difference in the relative singlet stability of over 10 kcal/mol between the two CpCr(NO)(NH$_2$)X model complexes required further investigation. Indeed, formal metathesis of the Cl$^-$ ligand in CpCr(NO)(NH$_2$)Cl with a CH$_3^-$ group unexpectedly resulted in a significantly greater relative change than the initial replacement of NH$_2^-$ for Cl$^-$ in CpCr(NO)Cl$_2$ (7.25 kcal/mol). Calculations were thus conducted on methyl-containing compounds in order to identify the source of the enhanced singlet stability.

Comparison of CpCr(NO)(CH$_3$)X (X = Cl, CH$_3$). As shown in Figure 3, triplet CpCr(NO)(CH$_3$)Cl is calculated to be 1.52 kcal/mol lower in energy than the singlet state. While this constitutes an improvement in relative singlet stability of more than 6 kcal/mol over the CpCr(NO)Cl$_2$ species, the change in energies is larger between CpCr(NO)Cl$_2$ and CpCr(NO)(NH$_2$)Cl or between CpCr(NO)(NH$_2$)Cl and CpCr(NO)(NH$_2$)CH$_3$. Formal substitution of a second methyl group leads to an even smaller relative difference. Singlet CpCr(NO)-(CH$_3$)$_2$ is the ground spin state, but it is calculated to be only 2.37 kcal/mol more stable than the triplet state.

In summary, the diamagnetic $S = 0$ state is favored by the X ligands in the order NH$_2$ > CH$_3$ > Cl. The presence of a chloride ligand attenuates the stability conferred by amide ligation but does not hamper the effects imparted by an alkyl group. Addition of a second alkyl group causes only a minor improvement in the relative energy of the $S = 0$ state, while combining amide and alkyl ligands appears to have an additive stabilizing effect.

π-**Donation and Orbital-Splitting Energy.** To identify the metal−ligand bonding interactions respon-

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(35) Similar paramagnetic complexes containing weak, dual-faced π-donor ligands have been observed for Cp*Mo(PMe$_3$)$_2$Cl[12] and CpMo-(PMe$_3$)$_2$(OH).[36]

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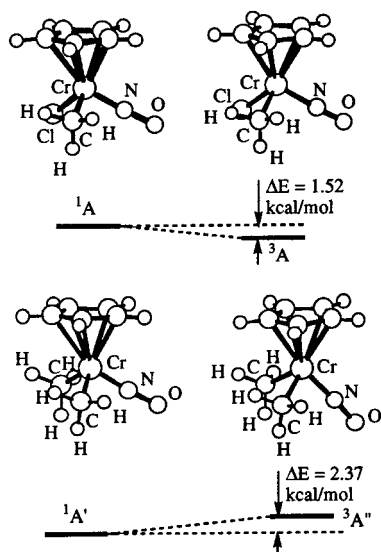
Figure 3. Relative energies and DFT-B3LYP-optimized geometries of ^{1}A and ^{3}A CpCr(NO)(CH$_3$)Cl and ^{1}A′ and ^{3}A″ CpCr(NO)(CH$_3$)$_2$.
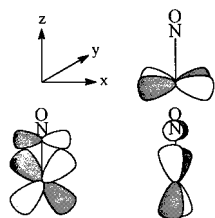
Figure 4. Pictorial representation of the NO π-bonding interactions in CpM(NO)X$_2$ (M = Mo, Cr).

sible for the differences in singlet vs triplet relative energies, extended Hückel molecular orbital calculations were performed on the B3LYP-optimized geometries of the CpM(NO)X$_2$ species. We have previously employed these low-level calculations to correlate experimentally determined reactivity and ligand π-bonding properties in related CpCr(NO)(ligand)$_2$ complexes.[20,31] By simplifying the bonding character of the frontier orbitals, the EHMO results provided valuable, qualitative insights into the source of the lengthened M–NO bonds calculated for the triplet CpM(NO)X$_2$ species and the ability of the amide ligand to stabilize the singlet state.

The spin-state dependence of the M–NO bond length can be explained by comparing the bonding character and occupancies of the valence orbitals of the generic CpM(NO)X$_2$ species. For the low-spin CpM(NO)X$_2$ complexes, the two highest occupied orbitals are both doubly occupied, mutually orthogonal, and strongly π-bonding to the nitrosyl ligand. All four of the valence electrons are therefore involved in the π-interaction that keeps the nitrosyl ligand bound to the metal. The LUMO is metal-centered, nonbonding, and roughly perpendicular to the M–NO axis. These orbitals are illustrated schematically in Figure 4. In the triplet CpM(NO)X$_2$ species, the metal-centered, nonbonding orbital is now singly occupied and the two M–NO π-bonding orbitals contain only *three* electrons. This reduction of M–NO bond order in the triplet state accounts for the relative lengthening and weakening of the M–NO bond. Understanding the underlying factors which trigger release of NO from transition metals is
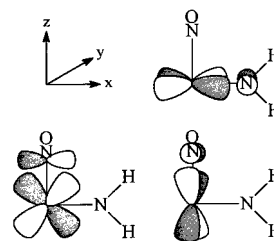
of potential significance to both the biological role of nitric oxide[37] and the rational design of transition-metal nitrosyl compounds as pharmaceutical agents.[33c,38]

Figure 5 illustrates why the ON–Cr–NH$_2$ group must be planar for a full Cr–N(amide) π-bond to form in CpCr(NO)(NR$_2$)X species. As in the case of singlet CpM-(NO)X$_2$, two filled orbitals are engaged in π-bonding to the nitrosyl ligand. The orbital perpendicular to the Cr–NO axis is empty and can accept π-donation from the filled amide N p orbital only when the amide ligand is coplanar with the Cr–nitrosyl bond.[20–22] The π-antibonding orbital shown in Figure 5 forms the LUMO of singlet CpCr(NO)(NH$_2$)X. The Cr–NH$_2$ π-bonding interaction is expected to raise the energy of the empty orbital perpendicular to the Cr–NO axis in CpCr(NO)-(NH$_2$)X relative to the analogous orbital in CpCr(NO)-Cl$_2$, leading to a comparatively larger HOMO–LUMO gap and an increased preference for the low-spin, singlet electronic configuration.

The planar arrangement of amide and nitrosyl ligands in CpCr(NO)(NH$_2$)X species is reminiscent of the ligand orientations observed in related d^4 and d^2 complexes which contain both π-donor and π-acceptor ligands.[39–42] The ability of π-donor ligands to stabilize unsaturated species has previously been noted for specific CpM(NO)-X$_2$ species[20,22,43] and has been reviewed for organometallic complexes in general.[44] The present results demonstrate that ligand π-bonding effects can also affect the relative energies of the spin states available to organometallic species through their influence on the orbital-splitting energy. This phenomenon is directly analogous to the ligand effects previously observed in the magnetic properties and UV/visible spectra of Werner-type coordination compounds, as empirically ranked in the spectrochemical series.[2]

The relevant π-bonding orbitals for triplet CpCr(NO)-(NH$_2$)Cl are illustrated schematically in Figure 6. The

Figure 5. Pictorial representation of the NO and NH$_2$ π-bonding interactions in singlet CpCr(NO)(NH$_2$)X (X = Cl, CH$_3$).

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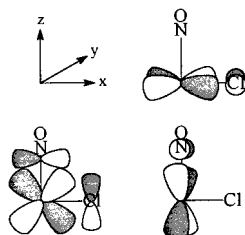
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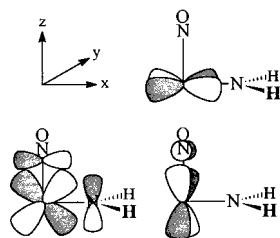
Figure 6. Pictorial representation of the NO and NH₂ π-bonding interactions in triplet CpCr(NO)(NH₂)X (X = Cl, CH₃).

Figure 7. Pictorial representation of the NO and Cl π-bonding interactions in CpM(NO)Cl₂ (M = Mo, Cr).

highest energy doubly occupied orbital is orthogonal to the amide and is Cr−NO π-bonding in character. The highest energy *singly* occupied orbital is orthogonal to the nitrosyl, is metal-centered, and is nonbonding. Between these two is a singly occupied orbital which is π-*bonding* to the NO and π-*antibonding* to the NH₂. The source of the lengthening of both the Cr−NH₂ and Cr−NO bonds in triplet CpCr(NO)(NH₂)Cl can be traced to the lower energy singly occupied orbital. Since this orbital is Cr−NH₂ antibonding, the Cr−amide bond order is decreased. Like triplet CpM(NO)X₂, there are only three electrons in the Cr−NO π-bonding orbitals, which again leads to a weaker bond to the nitrosyl ligand. Note that the HOMO is metal-centered and nonbonding and that no purely metal−ligand antibonding orbitals are occupied.

While chloride ligands are weaker π-donors than amide groups, the inability of Cl⁻ to stabilize the singlet spin state in CpCr(NO)Cl₂ may be attributed to the nature of the Cr−Cl π-bonds rather than their insufficient strength. A Cl⁻ ligand is a double-faced π-donor and therefore establishes π-interactions with two metal orbitals (d$_{xy}$ and d$_{xz}$ in Figure 7). The result is that it is equally efficient in transferring π-electron density to the metal in both spin states (one net Cr−Cl π-interaction + one filled−filled π-repulsion in the singlet state vs two two-center−three-electron interactions in the triplet state).

M−X Bond Covalency and Spin-Pairing Energy. While the ligand π-bonding effects revealed by EHMO calculations help rationalize the calculated singlet vs triplet relative energies of complexes containing amide and chloride ligands, the alkyl ligand effects are not amenable to such an analysis. The discrepancy between CpCr(NO)Cl₂ (triplet state more stable by 8.20 kcal/mol) and CpCr(NO)Me₂ (singlet state favored by 2.37 kcal/mol) in particular is difficult to reconcile with the known ability of chloride ligands to stabilize unsaturated compounds through π-donation.[44] The same counterintuitive trend was encountered for TiX₂(dmpe)₂, where the X = Cl species is paramagnetic[45] and the

isostructural X = CH₃ compound is diamagnetic.[46] Hall and co-workers demonstrated that this surprising result was due to differences in electron−electron repulsions in the two complexes.[32] The more electronegative Cl⁻ ligands increase the effective charge on the metal atom, leading to relatively contracted frontier orbitals and strong repulsions between paired electrons, resulting in a ground triplet state. The more covalent CH₃⁻ ligands cause the orbitals to be more diffuse, decreasing electron pairing energy and favoring the singlet state.

A quantitative analysis of the interelectron-repulsion energy in the CpM(NO)X₂ complexes was performed using the method developed by Hall et al.[32] The two relevant frontier orbitals φ_1^α and φ_2^α were extracted from the B3LYP calculations of the triplet state. The extremely long triplet M−NO bond lengths and the structural differences between the singlet and triplet optimized geometries preclude the accurate quantification of the singlet−triplet splitting from the values of $\Delta\epsilon$ (the orbital-splitting energy) and the Coulomb (J) and exchange (K) integrals, but the general trends exhibited by these integrals should yield important information regarding how the interelectron repulsion energy is influenced by the ligands. These J and K integrals are the "spin-pairing" relationships that the Racah parameters were originally formulated to approximate.[2,47] The values obtained for J_{11}, J_{12}, and K_{12} are collected in Table 4.

The overall "pairing energy" can be roughly described by the relation $J_{11} - J_{12} + K_{12}$, which is the difference between the Coulombic repulsions experienced by two electrons paired in the lower energy orbital φ_1^α (J_{11}) compared to two electrons each in separate orbitals φ_1^α and φ_2^α (J_{12}), plus the exchange energy (K_{12}). As expected, the value of $J_{11} - J_{12} + K_{12}$ is much smaller for CpMo(NO)Cl₂ than for CpCr(NO)Cl₂, due to the larger orbitals of the second-row transition metal Mo compared to the first-row Cr. This accounts for the dramatic stabilization of the singlet ground state relative to that calculated for the chromium species and so for the observed diamagnetic configuration of the Mo compound. The considerable decrease in $J_{11} - J_{12} + K_{12}$ along the series CpCr(NO)Cl₂ > CpCr(NO)(CH₃)Cl > CpCr(NO)(CH₃)₂ is consistent with the increasing covalency of the Cr−X bonds, leading to a decrease in pairing energy and subsequent relative stabilization of the singlet state. Hence, these results demonstrate that pairing energies mirror the intuitive picture of electron "cloud expansion" (i.e. the nephelauxetic effect), initially developed to explain the same phenomenon in Werner-type coordination compounds.[47] Somewhat expectedly, the J and K calculations yield inconsistent results for the amide complexes. The observed changes of conformation and electronic structure (e.g. Cr−NH₂ π-bonding), in addition to the variation in Cr−NO bond length, render the approximation of the singlet configuration by changing the occupation of the triplet orbitals completely unacceptable.

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Table 4. Monoelectronic Analysis of the Interelectron Repulsion Energies for 16-Electron CpM(NO)XY (M = Mo, X = Y = Cl, M = Cr, X, Y = Cl, CH₃, NH₂)[a]

	Mo/Cl$_2$	Cr/Cl$_2$	Cr/Cl/NH$_2$	Cr/CH$_3$/NH$_2$	Cr/Cl/CH$_3$	Cr/(CH$_3$)$_2$
J_{11}	268.80	1240.46	1251.60	1050.78	976.17	531.65
J_{12}	194.24	1134.98	805.95	797.88	966.79	697.64
K_{12}	20.16	67.36	41.70	97.95	65.35	27.07
$J_{11} - J_{12} + K_{12}$	94.72	172.84	487.35	350.85	74.73	−138.92

[a] All energies are expressed in kcal/mol.

Conclusions

The geometries and relative energies of CpM(NO)X$_2$ model compounds (M = Cr, Mo; X = Cl, NH$_2$, CH$_3$) have been calculated for both singlet (low spin, $S = 0$) and triplet (high spin, $S = 1$) electronic configurations using density functional techniques. The stability of compounds not yet directly observed (e.g. CpCr(NO)Cl$_2$) or even generated (e.g. CpCr(NO)(CH$_3$)$_2$) may thus be evaluated theoretically. The salient points resulting from this computational study are as follows:

(1) The discontinuity in CpM(NO)X$_2$ chemistry between Mo and Cr may be due to spin-state differences attributable to the increased interelectron repulsion present in the Cr species.

(2) CpCr(NO)Cl$_2$ is calculated to possess a triplet ground state.

(3) Adopting a high-spin, $S = 1$ configuration significantly lengthens the metal−nitrosyl bond in CpCr(NO)X$_2$ species due to promotion of an electron from a Cr−NO π-bonding orbital. The concomitant weakening of the Cr−NO bond provides a rationale for the nitrosyl-loss reactivity postulated for high-spin CpCr(NO)Cl$_2$.

(4) Formal replacement of Cl$^-$ with an amide ligand stabilizes the singlet state because of the enhanced Cr−NR$_2$ π-bonding relative to the triplet state. To a first approximation, Cr−Cl π-bonding is equivalent in both spin states.

(5) Formal alkyl-for-chloride metathesis stabilizes the diamagnetic configuration because of a decrease in pairing energy.

(6) The singlet-stabilizing bonding effects of the alkyl and amide ligands are complementary.

(7) Despite its electronic unsaturation (absence of π-donating ligands), CpCr(NO)(CH$_3$)$_2$ is calculated to have a ground singlet spin state. Attempts to synthesize diamagnetic CpCr(NO)(alkyl)$_2$ complexes are currently in progress.