EPR Spectroscopy

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Heterobimetallic Nitride Complexes from Terminal Chromium(V) Nitride Complexes: Hyperfine Coupling Increases with Distance**

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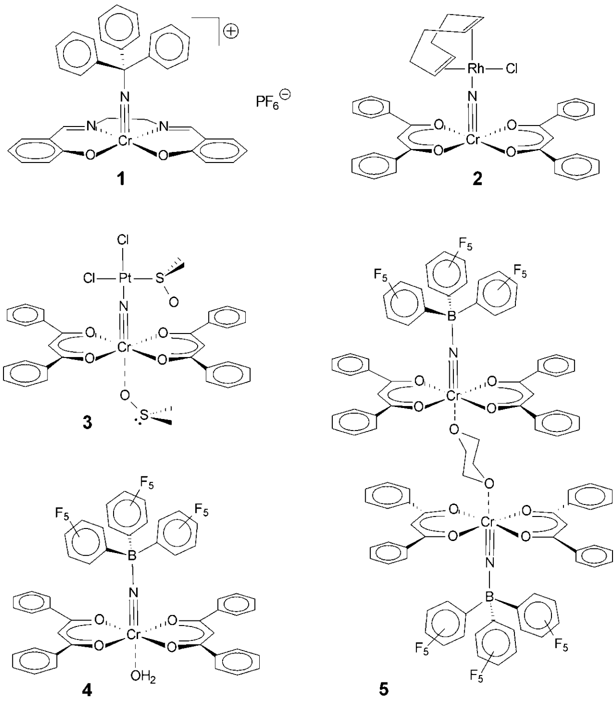
Terminal nitride complexes of rhenium, osmium and molybdenum can form complexes with either alkylating agents, Lewis acidic metal halides, or low-valent, coordinatively unsaturated metal complexes.[1–7] The few reactions of this type with a first-row transition-metal complex are limited to vanadium.[8,9] Recently, the nitride chemistry of the chromium(V) cation has been significantly expanded by introduction of a preparative route which is based on nitrogen transfer from [Mn(N)(salen)] (salen = *N*,*N'*-bis(salicylidene)ethylenediamine) to the chromium(V) cation.[10–12] With a range of chromium nitride complexes at hand we have investigated their reactivity and found that nucleophilicity is a general property which can be observed during formation of imide complexes with, for example, the trityl cation, tris(pentafluorophenyl)boron, and methyl triflate. In addition we report that terminal chromium(V) nitride complexes coordinate through the nitride ligand to low-valent complexes of the platinum metals. These compounds are possible precursors to bimetallic nitride phases which are gaining in importance as heterogeneous catalysts in, for example, the Haber–Bosch process.[13]

Solutions of terminal chromium nitride complexes in noncoordinating solvents treated with electrophiles such as $B(C_6F_5)_3$ or $C(C_6H_5)_3^+$ quickly yield intensely colored orange-red or green solutions. The reactions proceed cleanly as shown by EPR spectra which display a signal from a single $S = \frac{1}{2}$ spin species. Similar reactivity was observed in reactions with either $[Rh(cod)Cl]_2$ or *cis*-$[PtCl_2(dmso)_2]$ (cod = 1,5-cyclooctadiene, dmso = dimethyl sulfoxide). Structures of some of these systems, characterized by single-crystal X-ray diffraction, are shown in Scheme 1.



Scheme 1. Schematic representation of the chromium(V) imide and chromium(V) bridging-nitride complexes.

Experimental and crystallographic details such as ORTEP drawings and metric parameters of complexes **1**–**5** (Scheme 1) are available in the Supporting Information (Tables S1 and S1 a). Inspection of the structures reveals a number of general aspects: there is a strong propensity for the chromium center to increase its coordination number from five to six upon coordination of the nitride ligand. This propensity is expected and a consequence of the *trans* influence of either an imide or a bridging nitride ligand which is significantly lower than that of a terminal nitride ligand. Accompanying this, the displacement of Cr out of the plane spanned by the equatorial ligators is diminished from about 0.5 to about 0.2 Å. The Cr–N bond length is elongated from 1.55 Å in the terminal nitride complexes to approximately 1.60–1.62 Å in the functionalized systems. Comparison of structure **1** with that of [Cr(N)(salen)] reveals that the metal–salen ligand bonds are significantly shorter when the nitride ligand is functionalized, as expected when two ligands compete for electron donation. However, for the systems derived from $[Cr(N)(dbm)_2]$ the situation is less clear (dbm = dibenzoylmethanolate). In complex **2** all the Cr–dbm bonds are longer than in the parent terminal nitride complex, while they are shorter or similar within the limits of uncertainty in complex **5**. The B–N and C–N bonds in **1**, **4**, and **5** are unexceptional but the N–Rh and N–Pt bond lengths in **2** and **3** are at about 1.970 and 1.906 Å, respectively, and very short; the first value belongs to the top 5 % of the shortest Rh–N bonds and the second belongs to the top 1 % of the shortest Pt–N bonds. Table 1 compares the Pt–N bond of **3** with Pt–N bonds of other *cis*-$[PtCl_2(dmso)L]$ structures.

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Table 1: Bond lengths in *cis*-[$PtCl_2$(dmso)L].

L	Pt–N [Å]	Reference
NH_3	2.030	[14a]
pyridine	2.027	[14b]
pyrimidine	2.023	[14c]
CH_3CN	1.976	[14d]
C_2H_5CN	1.951	[14e]
$Cr(dbm)_2(N)$	1.9058	this work

These findings support the suggestion that terminal nitride complexes act as strongly π-electron-accepting ligands towards the electron-rich platinum metals. This suggestion was first proposed by Mayer and co-workers and is based on the spatial similarity of the lowest unoccupied molecular orbitals (LUMOs) of the Os≡N and C≡O bonds.[15]

It is well-documented that superhyperfine coupling in terminal nitride complexes of Cr^V is equal in magnitude for the tightly bonded nitride ligand (d(Cr–N) ≈ 1.55 Å) and the equatorial ligating nitrogen (d(Cr–-N) ≈ 1.9–2.0 Å).[16] This accidental degeneracy is caused by two compensating effects, that is, the bond length difference and the fact that the unpaired electron of the chromium(V) cation occupies a d_{xy} orbital which has no direct overlap with valence orbitals of the terminal nitride ligand but interacts through π bonding with the more distant equatorial ligating atoms. Measurement of the magnetic susceptibility of **1** between 50 and 300 K provided a temperature-independent magnetic moment of 1.9 BM which is close to that expected for a $S = {}^1\!/_2$ spin system and corroborates the formulation of **1** to be a Cr^V imide complex. The room-temperature solution EPR spectrum of **1** differs significantly from that of [Cr(N)(salen)]. It can be simulated with either 1) two large and one small or with 2) one large and two small isotropic hyperfine coupling constants to the nitrogen atoms (Figure 1). The former approach reproduces the line positions of the measured spectrum but not their relative intensities while the latter yields an entirely satisfactory simulation. In addition to conventional simulations we have also employed fittings of the complete spectral traces to parameterize the EPR spectra. Thereby, we obtained realistic uncertainties on the spin-Hamiltonian parameters and objective measures of the qualities of the fits which renders the assignments made for the nitrogen hyperfine coupling constants statistically unequivocal (Table S4 in the Supporting Information). The single nitrogen of the imide ligand (d(Cr–N) = 1.62 Å) has an isotropic superhyperfine coupling constant which is more than twice that of the terminal nitride ligand in the parent complex (d(Cr–N) = 1.559 Å) and it is counterintuitive. This finding, however, becomes irrefutable when the EPR spectra of the other systems **2–4** and that resulting from a reaction of $[Cr(N)Cl_4]^{2-}$ with CPh_3^+ are considered. In all of these systems the ^{14}N-hyperfine coupling to the single nitrogen is 170 to 250 % that of the terminal nitride complexes (Figure 2 and the Supporting Information).

Ligand hyperfine coupling is in principle external to ligand field theory, but it is tempting to speculate that the interaction of the unpaired electron in the metal d_{xy} orbital with the axial nitrogen ligand comes about by mixing of the

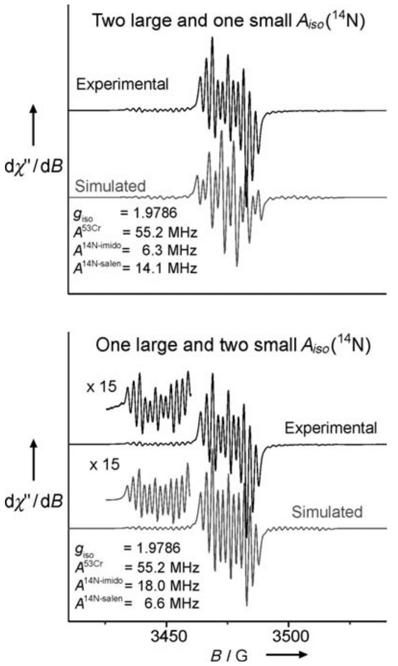

Figure 1. Experimental room-temperatutr solution X-band EPR spectrum of [Cr(N-CPh_3)(salen)]$^+$ in CH_2Cl_2 and its simulations. The upper simulation employs the intuitive choice of two large and one small nitrogen superhyperfine coupling while the lower simulation corresponds to the reverse situation of one large and two small nitrogen superhyperfine couplings. In the parent nitride complex, Cr(N)(salen), all three couplings are nearly identical in magnitude. The insert in the lower part of the figure is an expansion of one of the M_I components of the splitting caused by ^{53}Cr ($I = 3/2$; 9.5 % abundance).

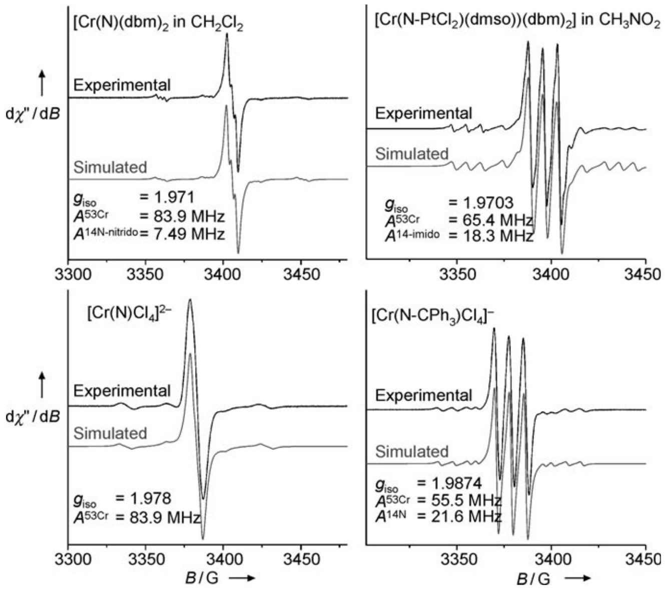

Figure 2. Experimental room-temperature solution EPR spectra of **3**, [Cr(N-CPh_3)Cl_4]$^-$, and their parent nitride complexes together with their simulations. See the Supporting Information for analogous spectra and their simulation for compounds **2**, **4**, [Cr(N)(salen)], [Cr(N)(tpp)], and imide as well as bridging-nitride complexes derived from the latter systems.

d_{xy} orbital with metal orbitals which can directly overlap with ligand orbitals. One possible mechanism could be spin–orbit coupling (SCO) admixture of the Cr–N π* set of orbitals $\{d_{xz},d_{yz}\}$ to the ground state. In a perturbation description this admixture would be inversely proportional to the $E(\{d_{xz},d_{yz}\})-E(d_{xy})$ energy separation which is dominated by the π interaction with the axial ligand. Based on spectroscopic data from the literature and the assumption that O^{2-} and $R-N^{2-}$ are comparable with respect to π-electron donation, the energy difference $E(\{d_{xz},d_{yz}\})-E(d_{xy})$ is expected to be approximately twice as large in the nitride complexes as in the imide analogues. This would accordingly justify the inverse ratio between the ^{14}N hyperfine couplings in the two classes of systems.

It has recently been shown independently by Kaupp et al.[17,18] and Neese[19] that DFT methods can yield insight into mechanisms and magnitudes of metal and ligand hyperfine coupling constants in transition-metal complexes. We have, along this venue, performed DFT calculations with the Orca program[20] on a range of model systems to gain more insight in the cause of the relative magnitude of the experimentally determined hyperfine coupling constants. As a model for the nitride complexes we use the experimentally determined geometry of $[Cr(N)(dbm)_2]$, which is the parent nitride complex of compounds **2**–**5**. We replaced the phenyl groups of the dbm ligand with hydrogens with a C–H bond length fixed at 0.96 Å. As a model for the functionalized complexes we used a linear methyl imide complex with an equatorial coordination sphere which is identical to that of our nitride model. Neese has tested different functionals and basis sets.[19] We follow his choice of the B3LYP functional combined with the VTZP basis supplemented with specially flexible bases suitable for describing the core properties (CP and IGLO-III, respectively) of Cr and N atoms. Details of the calculations and a sample input file are available in the Supporting Information.

The calculated values of the ^{14}N and ^{53}Cr hyperfine coupling constants for our nitride model are −10.1 and 75.7 MHz, respectively, for the experimental geometry ($d(Cr-N) = 1.56$ Å). For the imide model ($d(Cr-N) = 1.62$ Å), we obtained −47.3 and 44.4 MHz, respectively. The DFT method thus reproduces the much larger ^{14}N hyperfine coupling constants in the imide complexes. It should be noted that the quoted values are for calculations without inclusion of second-order SCO. We found, in agreement with our expectation and the findings of Neese, that inclusion of SOC has only a marginal effect on the magnitude of the chromium(V) hyperfine coupling and no effect on the nitrogen hyperfine coupling. We also tested the importance of lowering the symmetry by bending the Cr–N–C bonds in the imide model and found no significant (< 5%) change in the hyperfine coupling upon going from a linear geometry to a bent geometry (170° and 160°). We interpret the minimal effect of spin–orbit coupling and of lowered symmetry as signifying that the ligand field picture discussed above cannot be used to rationalize the observed variation of the hyperfine coupling constants. Instead we agree, based on the calculated ^{14}N hyperfine coupling constants, with Kaupp et al. that spin polarization in the strong Cr–N bonds is the main mechanism for the ligand superhyperfine coupling constants. It remains, however, counterintuitive that a spin-polarization mechanism should result in stronger coupling constants with increasing bond length. To verify whether the calculated difference between nitride and imide complexes was due to a difference in the nitrogen coordination environment or bond length we calculated the variation of the hyperfine coupling constants with Cr–N distances for both the nitride and imide complex keeping everything else constant. The Cr–N bond lengths were varied from 1.54 Å, which is just below the experimental distance in the nitride complexes, to 1.92 Å, which approaches the distance of a Cr–N single bond. The results are depicted in Figure 3.

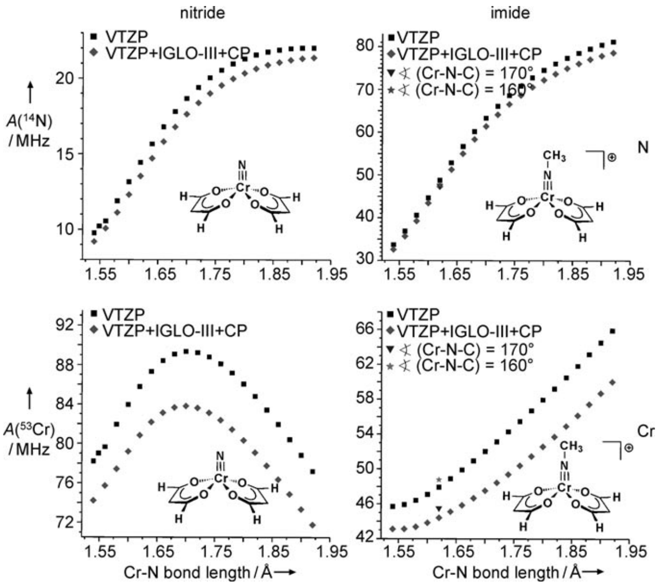

Figure 3. Calculated variation of the isotropic hyperfine coupling constants to nitrogen and chromium(V) as a function of the Cr–N bond length. The calculations employed the Orca program and the B3LYP functional. The results are obtained with a VTZP basis set for all atoms as well as with special basis sets adapted for description of core properties of Cr and N atoms. In addition, two points for each of the imide systems (at 1.62 Å) illustrate the relative lack of sensitivity towards bending of the Cr–N–C moiety (170°, 160°).

Surprisingly, the nitrogen hyperfine coupling constants increase quite steeply with the Cr–N distance for both classes of compounds. Examination of the calculated spin and charge densities reveals the cause of the paradox: as is the case for many simple compounds, the dissociation of chromium nitride (imide) complexes in the gas phase does not preserve the oxidation states Cr^{V} and N^{-III} but results instead in Cr^{III} and a triplet N^{-I} (Figure S7 and text in the Supporting Information). As a limiting result of a calculation this is rather unexceptional—the interesting fact is that this effect manifests even at equilibrium bond distances and that the present systems provide an exceptional case of an apparently simple system where the notion of well-defined spectroscopic oxidation states is experimentally challenged. Accordingly, Wieghardt and co-workers found the internal oxidation state distribution within a chromium imido fragment $\{Cr^{IV/III}$-

$(NAd)^{2-/-}\}^{2+}$ to depend on the oxidation state of the auxiliary noninnocent ligands.[21] This finding and our present study show that even ligands such as nitride and imide cannot be considered completely redox-innocent.

The facile coordination of the $\{Cr^{V}(N)\}^{2+}$ moiety in combination with the observed increase in the superhyperfine coupling to nitrogen renders this complex a promising spin probe for further EPR studies.

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