(Mes = 2,4,6-mesityl) with stoichiometric amounts of $(i\text{-Pr})_2NH$ or by reaction of $CrCl_2(thf)_2$[10b] with 2 equiv of $(i\text{-Pr})_2NLi$. The reaction is quite general, and the result is affected by the nature of the alkyl substituents of the amide moiety. While a complex isostructural with **1** has been isolated in the case of the bulky Cy_2N–(Cy = cyclohexyl), only monomeric square-planar species ($(R_2N)_2CrL_2$ and $(R_2N)_4CrLi_2L_2$: R = ethyl; L = 2 thf, py) have been obtained in the case of smaller substituents.[6c]

Complex **1** crystallizes in the triclinic space group $P\bar{1}$.[11] The unit cell contains two amide-bridged dimers (Figure 1). Each dimer has a slightly puckered central core of two chromium and two nitrogen atoms (deviation from the least-squares plane 0.012 (1) and 0.012 (3) Å). The geometry of the three-coordinated chromium atoms is severely distorted trigonal planar, and the two terminally bonded nitrogen atoms lie approximately in the same molecular plane. The molecular arrangement is quite similar to that of the previously reported $[(RO)Cr(\mu\text{-OR}')]_2$.[8] The Cr–N bond distances for the terminal and the bridging amido groups are quite different (Cr(1)–N(1) = 1.927 (3) Å, Cr(1)–N(3) = 2.065 (3) Å), in agreement with the two different coordination geometries (tetrahedral versus trigonal), which suggest a different nature of bonding to chromium. The trigonal-planar geometry of N(3) and N(4) indicates a strong nitrogen → metal π-interaction for the terminally bonded amino groups. In contrast, in the case of the bulky and monomeric $[(Me_3Si)_2N]_2Cr(thf)_2$[12b] and isostructural $\{[(Me_3Si)_2N]Mn[\mu\text{-N}(SiMe_3)_2]\}$,[12a] no such interaction has been claimed and the planarity of the nitrogen atoms has been explained in terms of nitrogen → silicon strong π-bonding interactions.

The value of the Cr···Cr intermetallic distance (Cr···Cr = 2.8657 (9) Å) falls between those observed for $Me_8Cr_2Li_4$[4b] and $(RO)_8Cr_2Na_4$[6] (1.98 and 3.634 Å, respectively) and indicates the presence of a Cr–Cr single bond only.[13] However, the magnetic properties of **1** support the idea that no real Cr–Cr bond actually occurs, in spite of the short intermetallic separation. The magnetic susceptibilities showed in fact a dependence on the temperature in the range 120–298 K, in agreement with the Curie–Weiss law. The presence of a strong antiferromagnetic interaction can be diagnosed by the large negative value of Θ ($\Theta = -101$ K).[14] The value of μ_{eff} ($\mu_{eff} = 2.30\ \mu_B$) is significantly lower than expected for a low-spin d^4 electronic configuration (μ_{eff} spin-only value 2.83 μ_B). These results can be explained by assuming either a low-spin d^4 electronic configuration of chromium (with only a strong antiferromagnetic interaction between the two metal centers) or a d^4 high-spin configuration with the two metal centers linked by a Cr–Cr double bond. Considering the high value of the intermetallic distance, this second possibility seems quite improbable.

Although the nature of the Cr–Cr interaction in complex **1** is not clarified by these results, an indication of the role played by the electron-donor ability of the bridging atom in affecting the size of the intermetallic separation emerges.

Further work to verify this point and to study the chemistry of Cr(II) amides is in progress at the moment.

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Supplementary Material Available: Tables of crystal data, positional and isotropic thermal parameters of non-hydrogen atoms, anisotropic thermal parameters of non-hydrogen atoms, positional parameters and isotropic thermal parameters of hydrogen atoms, bond distances, bond angles, and torsional angles (8 pages); a table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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(11) X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer for a crystal (0.5 × 0.5 × 0.5 mm) sealed in a Lindemann glass capillary: Zr-filtered Mo Kα radiation; triclinic, space group $P\bar{1}$, $a = 9.755$ (1) Å, $b = 10.731$ (1) Å, $c = 15.011$ (2) Å, $\alpha = 93.34$ (1)°, $\beta = 101.83$ (1)°, $\gamma = 100.18$ (1)°, $V = 1506.5$ (3) Å^3, $Z = 2$, $d_{calcd} = 1.113$ g cm^{-3}; $F(000) = 552$, μ(Mo Kα) = 7.2 cm^{-1}. The structure was solved with Patterson techniques (SHELXS 86) and refined with full-matrix least squares (SHELX 76) to a final $R = 0.049$ ($R_w = 0.071$, $S = 0.91$, $w = 1/\sigma^2(F_o)$, $\rho_{max} = 0.38$ e Å^{-3}, maximum shift/error = 0.2; 309 parameters (including anisotropic thermal parameters for the non-hydrogen atoms and two isotropic thermal parameters for the hydrogen atoms), 3784 reflections with $I > 2.5\sigma(I)$). Hydrogen atoms were introduced on calculated positions. One of the two isopropyl groups bonded to N(4) is probably disordered.

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Use of Bis(2,2′-bipyridyl-d_8)ruthenium(II) Dichloride To Facilitate NMR Structural Assignments in Complexes with Diimine Ligands

Over the past decade the field of ruthenium polypyridine chemistry has seen explosive growth due largely to the promise of such systems to act as effective photoredox catalysts.[1] Many of the complexes examined in this regard are of the general type $Ru(bpy)_2LL'^{2+}$ where LL′ is an unsymmetrical dimine ligand.[2] These complexes are relatively simple to prepare by treating the appropriate ligand LL′ with $Ru(bpy)_2Cl_2$ in refluxing aqueous ethanol. Characterization of the resulting complex by ^1H NMR spectroscopy is complicated by its lack of symmetry in that the two bpy ligands will give rise to 16 nonequivalent protons in addition to those associated with LL′. This problem has been recognized by previous workers, and a significant effort has been directed toward interpretation of these spectra[3] or the employment of two-dimensional techniques to facilitate assignments.[4]

We have recently developed a simple and straightforward solution to this problem: the utilization of bpy-d_8 as an auxiliary ligand in place of its protio analogue. This perdeuterio species can be prepared[5] simply by treatment of the corresponding di-*N*-oxide with NaOD in D_2O.[6] If 1.88 g of 2,2′-bipyridine

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(5) This material is also commercially available from MSD Isotopes, 2.5 g/$925.00.

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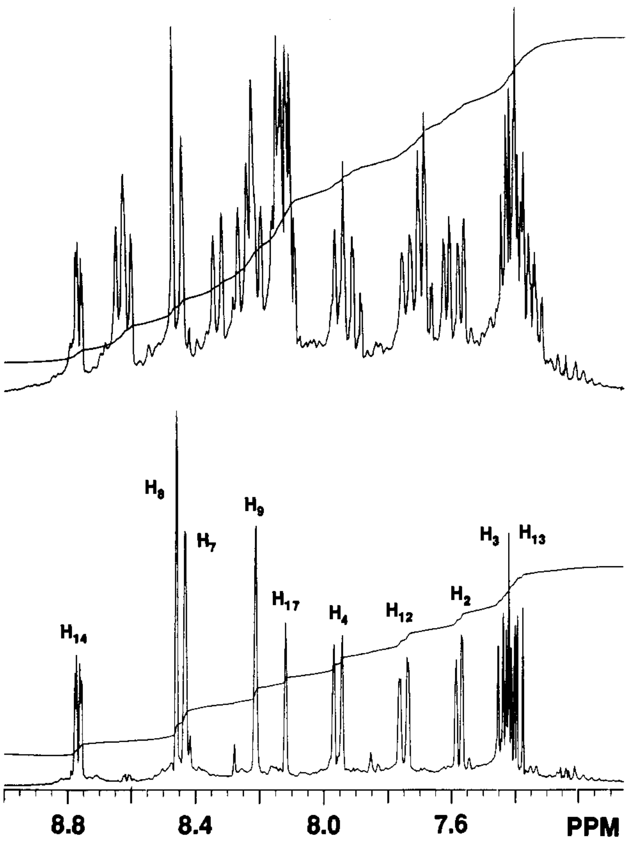
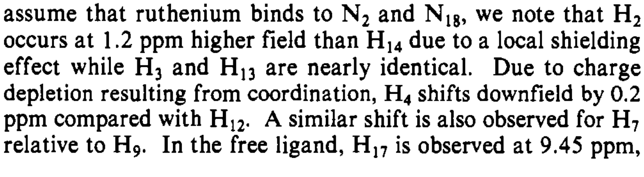


Figure 1. Downfield regions of the ^1H NMR spectra of $[Ru(1)(bpy)_2][PF_6]_2$ (top) and $[Ru(1)(bpy\text{-}d_8)_2][PF_6]_2$ (bottom) recorded at 300 MHz in CD_3CN.

1,1′-dioxide is treated twice successively with 0.73 g of sodium metal dissolved in 25 mL of D_2O (99.9 atom % D) followed by reduction of the perdeuterio di-*N*-oxide with PCl_3, 1.2 g (73%) of bpy-d_8 can be prepared. Mass spectral analysis indicated greater than 99% overall deuterium incorporation. The reaction of bpy-d_8 with $RuCl_3\cdot3H_2O$ according to a literature procedure[7] provided $Ru(bpy\text{-}d_8)_2Cl_2\cdot2H_2O$ in 63% yield.

To illustrate the utility of this new reagent, we have used it to prepare a mononuclear complex from a recently synthesized ligand with two equivalent bidentate sites: 5,6,10,11-tetrahydro-16,18-diazadipyrido[2,3-*a*:3′,2′-*n*]pentacene (**1**).[8] Figure 1 illustrates the ^1H NMR spectra of both the protio and deuterio analogues of this complex.



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2 a $[Ru(1)(bpy)_2][PF_6]_2$
b $[Ru(1)(bpy\text{-}d_8)_2][PF_6]_2$

When the 16 signals due to the nonequivalent bpy protons are eliminated, the spectrum of the coordinated **1** becomes quite interpretable. By comparison with previously established chemical shift values for ruthenium(II) complexes with bridged derivatives of 2,2′-bipyridine[9] and 2,2′-biquinoline,[10] nearly unambiguous assignments of the 10 remaining signals can be made. If we assume that ruthenium binds to N_2 and N_{18}, we note that H_2 occurs at 1.2 ppm higher field than H_{14} due to a local shielding effect while H_3 and H_{13} are nearly identical. Due to charge depletion resulting from coordination, H_4 shifts downfield by 0.2 ppm compared with H_{12}. A similar shift is also observed for H_7 relative to H_9. In the free ligand, H_{17} is observed at 9.45 ppm, while in the complex, it is strongly shielded and shifted upfield by 1.35 ppm. The diminished intensity of this signal, due to the long relaxation time of H_{17}, is also observed in the spectrum of the free ligand and assisted in its chemical shift assignment.

To verify that the use of bpy-d_8 would not cause an isotope effect on the ^1H chemical shifts, we compared $Ru(bpy\text{-}d_8)_2(bpy)^{2+}$ with $Ru(bpy)_3{}^{2+}$. Both compounds gave virtually identical ^1H NMR spectra at 300 MHz in CD_3CN.

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Photoelimination of Benzoyl Chloride from Benzoylchlorobis(triphenylphosphine)palladium(II) and -platinum(II)

The reductive elimination of acetyl iodide from a rhodium(III) intermediate is one of the basic steps of the Monsanto acetic acid synthesis,[1] but in comparison to oxidative-addition and migratory insertion reactions, very little is known about the reductive elimination of carboxylic acid halides.[2] We report in this paper the photoinduced reductive elimination of carboxylic acid chlorides, RCOCl, from *trans*-$[M(PPh_3)_2Cl(RCO)]$ (M = Pd, Pt) and $[Pt(LL)Cl(PhCO)]$ (LL = COD, dppe) in the presence of PPh_3 and CS_2. The photoelimination of RCOCl is unique because the photolysis of acylmetal complexes typically results in the loss of a ligand and subsequent migration of CO to the metal.[3] Substitution of CO by PPh_3 rather than migration takes place when $[Fe(C_5H_5)(CO)_2(CH_3CO)]$ is photolyzed in the presence of PPh_3.[4] While the photocleavage of metal–carbon bonds in metal alkyl complexes is well established,[5] the photocleavage of the metal–acyl carbon bond has not been previously demonstrated.

The acyl complexes *trans*-$[M(PPh_3)_2Cl(RCO)]$ are decarbonylated when heated at high temperatures.[6] A solution of *trans*-$[Pd(PPh_3)_2Cl(PhCO)]$ (**1**) and PPh_3 in dichloromethane that was stirred for 88 h gave no indication of reaction. The infrared spectra of a solution of **1** and PPh_3 in dichloromethane that was irradiated (450-W Ace-Hanovia medium-pressure ultraviolet lamp fitted with a quartz sleeve) are shown in Figure 1. The reaction proceeds with decay of the band at 1620 cm^{-1} due to **1** and concomitant growth of bands at 1772 and 1729 cm^{-1}, which are due to benzoyl chloride. The characteristic doublet band for benzoyl chloride, which was previously noted by Bellamy, was attributed to Fermi resonance.[7] The photoelimination of acetyl

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