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HAL Id: hal-03375382
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Received May 20, 1996

Sodium reduction of (ring)NbCl4 in the presence of the appropriate phosphine ligand affords the 16-electron Nb(III) complexes (ring)NbCl4L2 (ring = CsH5, L2 = dppe or ring = CsH5Me, L = PMe3). While the previously reported Cp*NBCl2(PMe3)2 complex behaves as a Curie-Weiss spin triplet paramagnet, compound (CsH5Me)NBCl2(PMe3)2 has a spin singlet ground state and a thermally populated excited triplet state (2.3 kcal/mol higher in energy) and (CsH5)NBCl2(dppe) is essentially diamagnetic. The X-ray structure of (CsH5Me)NBCl2(PMe3)2 shows a four-legged piano stool geometry, with Cl—Nb—Cl and P—Nb—P angles correlating with the experimentally determined singlet ground state. Theoretical calculations with geometry optimization at the MP2 level on both A" and A" states for the (CsH5)NBCl2-(PH3)2 model system confirm the strong dependence of the angular parameters on the spin state.

Introduction

Half-sandwich compounds with four monodentate ligands typically show the four-legged piano stool structural motif.1-3 Given the 14 electrons located in the metal—ligand bonds, this structure is allowed for metal centers with electronic configurations d0 through d4, to afford complexes with a total electron count of 14 through 18. For the 16-electron (d6) configuration, the four-legged piano stool structure has been verified crystallographically for compounds of group 4 metals in the oxidation state II, e.g. (C5H5)ZrCl2(L2)2 (L = Ph, Hf; X = Cl, Br, I)4,5 and (η5-arene)M[η6-arene]MCl2X2 (η6-arene = toluene; M = Zr, Hf; X = Cl, Br, I)4,5 for the V(III) compound CpCl2(PMe3)2,6 and for a few Mo(V) systems, e.g. [CpMoCl2(PMe3)2]4 and Cp*MoCl2-(PR3)2 (PR2 = PMe3, PMePh2).7-9 The group 4 M(II) complexes are all diamagnetic, whereas the isoelectronic V(III) and Mo(V) complexes are all spin triplet paramagnets. An analysis of the structural details of these molecules, especially the angle between the M—L bonds and the vector joining the metal with the center (CNT) of the ring, suggests a dependence on the spin state of the molecule. Although all molecules are of the four-legged piano stool type, independent of the spin state, the CNT—X angles (X = π donor ligand) are larger for spin singlet molecules (in the range 125°–130°) relative to spin triplet molecules (in the range 111°–118°); see Table 1. This difference has been ascribed to the better overlap of the proper symmetry X lone pair with the empty dπ orbital in the spin singlet compounds.2

Several half-sandwich compounds of group 5 metals in the oxidation state III are known, all those of vanadium being paramagnetic, e.g. CpVX2(PR3)2 (X = Cl, alkyl).10,13,14 For systems of Nb(III), on the other hand, there are no reported structures and no detailed magnetic studies. Compound Cp*NBCl2(PMe3)2 exhibits contact shifted 1H-NMR resonances, which led to the hypothesis of a spin triplet ground state.15 Similar shifts were subsequently observed for Cp*NBCl2(PMe2Ph2) with a magnetic susceptibility of 2.54 μB. However, no variable-temperature magnetic or NMR studies (which could probe the possible thermal population of excited states with a different spin) were reported.16 In addition, the NMR properties of the latter compounds were interpreted as consistent with a pseudo-trigonal bipyramidal structure, which, although established for the d6 complex [Cp*WMe4]4, would be unprecedented for a d8 system.

1† Dedicated to the memory of Sir Geoffrey Wilkinson.
18 (16) de la Mata, J.; Galakhov, M. V.; Gomez, M.; Rroyo, P. Organometallics 1993, 12, 1189–1192.
ligands.

the nature of the ground state for this class of deriva-

tive is ambiguous, and it is possible that the ground state

could involve up to three or four orbitals. However,

agent prior to use (THF and Et2O from Na/benzophenone,

atmosphere of argon. Solvents were dehydrated by conven-

tional means and dried under vacuum.

Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. J. Chem. Soc.,


Table 1. Angular Parameters (deg) in Spin Singlet and Triplet 16-Electron Four-Legged Piano Stool Compounds of Type trans-[ring]MX3L2

<table>
<thead>
<tr>
<th>compd</th>
<th>S</th>
<th>CNT–M–X</th>
<th>CNT–M–L</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(η⁵-toluenyl)ZrCl2(PMe2)2</td>
<td>0</td>
<td>125.3(1)</td>
<td>109.4(1)</td>
<td>9</td>
</tr>
<tr>
<td>(η⁵-C₅H₅)ZrCl2(PMe2)₂</td>
<td>0</td>
<td>130.1(1)</td>
<td>108.9(1)</td>
<td>8</td>
</tr>
<tr>
<td>CpVCl2(PMe3)2</td>
<td>1</td>
<td>117.0(0)</td>
<td>113.7(0)</td>
<td>10</td>
</tr>
<tr>
<td>[CpMoCl2(PMe3)2]⁺</td>
<td>1</td>
<td>118.5(1)</td>
<td>113.2(1)</td>
<td>11</td>
</tr>
<tr>
<td>[CpMoCl2(PMe3)2]⁻</td>
<td>1</td>
<td>110.9(1)</td>
<td>121.6(1)</td>
<td>43</td>
</tr>
</tbody>
</table>

α C₅H₅ = cycloheptatriene. β C₅H₅SiMe3 = (trimethylsilyl)cycloheptatriene.

Table 2. NMR Data

<table>
<thead>
<tr>
<th>complex</th>
<th>NMRa</th>
<th>1H (δ, ppm)</th>
<th>31P (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 290 K</td>
<td>54.7 (b, w1/2 = 893 Hz, Cp')</td>
<td>2.20 (b, w1/2 = 56 Hz, Pdemail</td>
<td></td>
</tr>
<tr>
<td>21 (b, w1/2 = 7100 Hz, Pdemail)</td>
<td>T = 283 K</td>
<td>8.4–7.3 (m, 10 H, Ph2P)</td>
<td>41.4 (s, dppe)</td>
</tr>
<tr>
<td>6.6–5.5 (m, 10 H, Ph2P)</td>
<td>5.87 (s, 5 H, Cp)</td>
<td>3.20 (m, 2 H, PCH2CH2)</td>
<td>2.95 (m, 2 H, PCH2CH2)</td>
</tr>
</tbody>
</table>

αThe solvent for all NMR determinations was C6D5CD3.

For these reasons, we have prepared and structurally

and magnetically characterized more examples of half-

sandwich Nb(III) compounds. The results of our studies

reveal the ubiquitous four-legged piano stool structure

for Cp'NbCl2(PMe3)2 (Cp' = η⁵-C₅H₅Me) and show that

the nature of the ground state for this class of derivatives

depends very delicately on the nature of the ligands.

Experimental Section

General Data. All operations were carried out under an

atmosphere of argon. Solvents were dehydrated by conven-
tional methods and distilled directly from the dehydrating

agent prior to use (THF and Et2O from Na/benzophenone,

heptane and toluene from Na, and CH2Cl2 from P2O5). NMR

spectra were recorded on Bruker WP200 and AF200 spectrom-

eters; the peak positions are reported with positive shifts

downfield of TMS as calculated from the residual solvent peaks.

The solvent for all NMR determinations was C6D5CD3.

Table 3, and selected bond distances and angles are collected

calculations, but not refined. Crystal data are reported in

structure was then refined by alternating least-squares cycles

position of the Nb atom was obtained from the analysis of the

Patterson map, and the positions of all the other heavy atoms

collected with wR2, % 8.08

Table 4. Crystallographic Data for 1

<table>
<thead>
<tr>
<th>formula</th>
<th>C8H22Cl2NbP2</th>
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<tbody>
<tr>
<td>fw</td>
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<tr>
<td>crys. size (mm)</td>
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<tr>
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<tr>
<td>space group</td>
<td>P21/n</td>
</tr>
<tr>
<td>a, Å</td>
<td>8.0735(5)</td>
</tr>
<tr>
<td>b, Å</td>
<td>13.9677(9)</td>
</tr>
<tr>
<td>c, Å</td>
<td>20.458(2)</td>
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<td>β, deg</td>
<td>90.3421(7)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>2306.9(3)</td>
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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Dcalc, g/cm³</td>
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<tr>
<td>μ(Mo Kα), Å</td>
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<tr>
<td>μ(Mo Kα), mm⁻¹</td>
<td>0.420</td>
</tr>
<tr>
<td>temp, K</td>
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</tr>
<tr>
<td>θmax, deg</td>
<td>24.7–22.47</td>
</tr>
<tr>
<td>data coll'd (hkl)</td>
<td>±8, –15, +22</td>
</tr>
<tr>
<td>no. refl's</td>
<td>3091</td>
</tr>
<tr>
<td>refinement method</td>
<td>full-matrix least-squares on F²</td>
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<td>data/est/param</td>
<td>2995/0/215</td>
</tr>
<tr>
<td>GOF</td>
<td>1.038</td>
</tr>
<tr>
<td>R1, %</td>
<td>4.98</td>
</tr>
<tr>
<td>wR2, %</td>
<td>8.08</td>
</tr>
</tbody>
</table>

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 1

| Nb–Cl(1) | 2.464(2) | Nb–P(2) | 2.638(2) |
| Nb–Cl(2) | 2.458(2) | Nb–CNTa | 2.018    |
| Nb–P(1)  | 2.625(2) |

C(2)–Nb–Cl(1) 114.38(7) P(1)–Nb–P(2) 149.86(7) |
C(2)–Nb–P(1) 81.66(7)  C(1)–Nb–CNTa 116.9 |
C(1)–Nb–P(2) 82.46(7)  C(2)–Nb–CNTa 128.7 |
C(1)–Nb–P(2) 80.95(7)  C(1)– Nb–CNTa 104.6 |
C(1)–Nb–P(2) 81.61(7)  P(2)–Nb–CNTa 106.3 |

a CNT is the center of gravity for C(1)–C(5).

Synthesis of CpNBCl2(dppe) (2). CpNBCl2 (0.637 g, 2.12 mmol) was added to a THF solution (40 mL) of amalgamated Na (0.104 g, 4.52 mmol in 10 g of Hg) and dppe (0.845 mL, 2.12 mmol). The solution was initially red and turned purple upon stirring for 0.5 h at room temperature. Stirring was continued for 2 days, during which time the solution turned dark red. The solution was evaporated to dryness, the residue was extracted with CH2Cl2 (3 × 5 mL), and the extracts were filtered through Celite until the washings were colorless. The CH2Cl2 solution was then concentrated to approximately 1/5 the initial volume and heptane (15 mL) was added, precipitating a red-brown solid. The solid was filtered off, washed with heptane (2 × 5 mL), and dried under reduced pressure. Yield: 0.534 g, 45%. Anal. Calc'd for C31H54Cl2NbP2: C, 59.3; H, 4.7. Found: C, 58.7; H, 4.6.

X-ray Analysis of Compound 1. Single crystals were obtained by cooling a concentrated heptane solution of 1 to –80 °C. A single crystal was glued to the inside of a thin-walled glass capillary, which was then flame sealed under dinitrogen and mounted on the diffractometer. The cell parameters and crystal orientation matrix were determined from 25 reflections in the range 13.1 < θ < 18.5°; these constants were confirmed with axial photographs. Data were collected with ω/2θ scans over the range 2.0 < θ < 22.5°. The position of the Nb atom was obtained from the analysis of the Patterson map, and the positions of all the other heavy atoms (Cl and P) were revealed by a subsequent DIRDIF run. The structure was then refined by alternating least-squares cycles and difference Fourier maps, revealing the positions of all other non-hydrogen atoms, to convergence with all non-hydrogen atoms anisotropic. Hydrogen atoms were finally included in calculated position and used for structure factor calculations, but not refined. Crystal data are reported in Table 3, and selected bond distances and angles are collected in Table 4.
Theoretical Calculations. Calculations were carried out with the Gaussian 94 package. The geometry optimizations were carried out with the LANL2DZ basis set without polarization basis functions, which include both Dunning and Hay's D95 sets for H and C and the relativistic ECP sets of Hay and Wadt for the heavier atoms. Electrons outside of the core were all those of H and C atoms, the 4s, 4p, 4d, and 5s electrons in the Nb atom, and the 3s and 3p electrons in Cl and P atoms. The input coordinates for the CpNbCl2(PH3)2 model compound were adapted from the X-ray structure of compound 1, which was idealized to C2 symmetry. The mean value of the spin of the first-order electron wave function, which is not an exact eigenstate of $S^2$ for unrestricted Hartree-Fock calculations on open-shell systems, was considered to identify unambiguously the spin state. The value of $<S^2>$ for the UHF calculation on the triplet state was 2.0274 at convergence, indicating minor spin contamination. A single-point energy calculation on the geometry optimized as described above was also carried out for both spin states by using the same functions for H, C, and Nb atoms, and the 6-311G basis set supplemented with diffuse functions and 3 sets of f polarization functions for the Cl and P atoms. The value of $<S^2>$ for the UHF calculation on the triplet state in this case was 2.0285.

Results

Synthetic Studies. Compounds with the general formula (ring)NbCl2L2 [ring = CsH4Me (Cp'), L = PEt3; (1); ring = Cp, L2 = dppe (2)], which are formally 16-electron, d2, Nb(III) complexes, have been synthesized by reducing (ring)NbCl4 in the presence of 2 equiv of crystalline materials and characterized by 1H- and 31P-NMR spectroscopy and by elemental (C, H) analysis. Compounds with the general formula (ring)NbCl2L2 were also characterized by X-ray crystallography. Compounds with the general formula (ring)NbCl2L2 + 2NaCl (1)

$$\text{(ring)NbCl}_2\text{L}_2 + 2\text{NaCl}$$

Half-sandwich compounds of Nb(III) with phosphine ligands that are already reported in the literature are described above. The 16-electron type for bulkier systems, e.g. Cp* NbCl2(PMe2Ph)2 (18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J. J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andzelm, J. J.; Repp, E. S.; Gomperts, R.; Martin, L. R.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94 (Revision A1); Gaussian Inc.: Pittsburgh, PA, 1995.


recently described CpMoCl2(PEt3)2 results in the observation of a shortening of the M–P bonds (2.632–(2) Å for 1 versus 2.532(1) Å for the Mo analogue), which can be partially attributed to the larger covalent radius of the Nb(III) versus the Mo(III). A smaller effect is observed for the M–CNT bond length with 2.018(2) Å for Nb–CNT in 1 and 1.940(2) Å for the Mo–CNT in CpMoCl2(PEt3)2. An 18-electron CpNBu(II) isocyanide complex, Cp*NbCl2(CN-2,6-Me2C6H3), has also been crystallographically characterized, and a Nb–CNT bond length was found to be 2.099(5) Å, which is slightly longer than that found for 1. In contrast to these observations, the average M–Cl bond distance is slightly shorter for the Nb complex (2.461(2) Å versus 2.476(1) Å for the Mo analogue). The 18-electron Nb isocyanide complex, Cp*NbCl2(CN-2,6-Me2C6H3), shows a significantly longer Nb-Cl bond, 2.561(2) Å. All these trends may be explained on the basis of changes in M–Cl and M–PEt3 π-bonding. The M–PEt3 π-back-bonding interaction is favored by a greater number of electrons in the metal-based orbitals (3 for Mo(III) and 2 for Nb(III)), whereas the M–Cl π-interaction is favored by a smaller number of electrons in the metal-based orbitals. For the 18-electron Cp*NbCl2(CN-2,6-Me2C6H3), there are no empty metal orbitals available for the establishment of a Nb–Cl π-interaction. Another interesting difference between the CpMCl2(PEt3)2 (M = Nb, Mo) structures concerns the CNT–M–L angles. The two CNT–Nb–Cl angles (116.9(1) and 128.7(1)°) are quite different from each other, presumably because of a steric repulsion of the Cp’ methyl group on the chlorine atom which is eclipsed with it (see Figure 1b). The Mo system, having a Cp ring, does not experience the same steric repulsion, and therefore the angles are similar (118.0(1) and 121.6(1)°). The average CNT–M–Cl angle for both systems is comparable (122.8(1)° for the Nb and 119.8(1)° for the Mo system). This angle, however, is significantly greater with respect to the corresponding angle of the iso electronic vanadium system, CpVCl2(PMe3)2. As stated in the Introduction, this angle appears to be diagnostic of the spin state (see Table 1); the angle observed for compound 1 falls in between those observed for diamagnetic compounds and for compounds that have two unpaired electrons, warranting further magnetic investigations by variable-temperature NMR spectroscopy.

NMR Studies. The magnetic properties of compounds 1, 2, and the previously reported15,16 Cp*NbCl2(PMe3)2 were probed by variable-temperature 1H-NMR studies. For compound Cp*NbCl2(PMe3)2, the contact-shifted resonances for both the Cp* and the PMe3 protons further shifted away from the diamagnetic region upon cooling. The observed linearity of the plots of δ versus 1/T (see Figure 2) is consistent with Curie–Weiss behavior for a spin triplet paramagnet. For compound 2, on the other hand, a temperature-independent 1H-NMR spectrum in the normal region (see Table 2) indicates a pure diamagnetic system. No resonances were observed in the 31P-NMR spectrum at room temperature, but a singlet resonance at δ 41 becomes observable upon cooling to 283 K. The latter phenomenon could be attributed to a fast relaxation of the phosphorus atom due to the vicinity of the quadrupolar Nb nucleus (I = 9/2, 100% abundance, Q = −0.366–(18) x 10−24 cm2, vs Q = −0.00282(19) x 10−24 cm2 for 2H). A possible slight population of a paramagnetic excited state is ruled out, since the position of the 31P-NMR resonance does not shift upon further cooling to 213 K. Few diamagnetic Nb phosphine compounds appear to have been investigated by 31P-NMR spectroscopy, and these commonly exhibit broad resonances at room temperature.25,30,31

As mentioned above, preliminary room-temperature 1H-NMR studies indicate paramagnetism for compound 1. The resonance at 59.7 ppm is tentatively assigned to the Cp’ methyl protons, while the Cp ring protons do not appear to be visible in the 1H-NMR spectrum. This is the same phenomenon previously observed for (ring)MoCl3L compounds: the Cp protons (e.g. for CpMoCl3(PMe2Ph)) are not observed in the 1H-NMR spectrum, while the Cp* protons for Cp*MoCl3(PMe2Ph) are observed at δ 0.6. The two additional resonances at δ −21 and 2.20 for 1 are tentatively assigned to the methane and methyl protons of the PET3 ligand, respectively. Lowering the temperature, however, resulted in a shift of all resonances toward the diamagnetic region, contrary to the case of Cp*NbCl2(PMe3)2. This phenomenon is consistent with a singlet ground state (as suggested by the X-ray structure) and a thermally populated triplet excited state. According to the literature, the temperature-dependent chemical shifts for a spin singlet/triplet equilibrium system are related to fundamental molecular properties as shown in eq 2.33–35

\[
\delta_{obs} = \delta_{dia} + \frac{g^2I_H A}{3kT(\gamma_H/2\pi)} \frac{6e^{-EAT}}{1 + 3e^{-EAT}}
\]

The constants in eq 2 have their usual meanings, while δdia is the non-contact-shifted chemical shift, A is the hyperfine electron coupling constant, and E is the

The unperturbed diamagnetic shifts, with those of free PEt3 and no new resonances in the hypothetical 18-electron Cp

δ determination of the parameters phosphine methyl resonance giving Cp

pling constant. This trend was observed for electronic coupling constant depends on the interaction of resonances, superimposed to the curve fits. The electronic coupling constant depends on the interaction of the nucleus with the unpaired electron; thus a more contact-shifted peak is expected to have a larger coupling constant. This trend was observed for 1, with the Cp’ methyl resonance yielding $A = -14(2)$ MHz and the phosphine methyl resonance giving $A = -0.4(2)$ MHz. The unperturbed diamagnetic shifts, $\delta_{\text{dia}}$, are 1(2) and 0.8(4) ppm, respectively, for the Cp’ methyl and PEt3 methyl protons. These values are in agreement with expectations for the chemical shifts of such protons in a diamagnetic environment, supporting the resonance assignment.

The addition of excess free PEt3 to solution of compound 1 did not show any evidence for coordination with formation of a (diamagnetic) 18-electron compound. The $^1$H-NMR spectrum of a solution of compound 1 to which was added a large excess of free PEt3 showed only the unperturbed resonances of 1 together with those of free PEt3 and no new resonances in the diamagnetic region that could be attributable to the hypothetical 18-electron Cp’NbCl2(PEt3)3. This result rules out both the presence of a significant amount of singlet–triplet energy gap.36–40 Using the Curve Fit program,41 a nonlinear least-squares fitting (quasi-Newtonian method) of the data to eq 2 allows the determination of the parameters $\delta_{\text{dia}}$, A, and E. Two of the resonances were sufficiently sharp to allow accurate measurements and independently yielded an identical energy gap within the experimental error [2.24(11) and 2.3(7) kcal/mol], as expected. Figure 3 shows plots of the chemical shift versus temperature for these two resonances, superimposed to the curve fits. The electronic coupling constant depends on the interaction of the nucleus with the unpaired electron; thus a more contact-shifted peak is expected to have a larger coupling constant. This trend was observed for 1, with the Cp’ methyl resonance yielding $A = -14(2)$ MHz and the phosphine methyl resonance giving $A = -0.4(2)$ MHz. The unperturbed diamagnetic shifts, $\delta_{\text{dia}}$, are 1(2) and 0.8(4) ppm, respectively, for the Cp’ methyl and PEt3 methyl protons. These values are in agreement with expectations for the chemical shifts of such protons in a diamagnetic environment, supporting the resonance assignment.

The addition of excess free PEt3 to a solution of compound 1 did not show any evidence for coordination with formation of a (diamagnetic) 18-electron compound. The $^1$H-NMR spectrum of a solution of compound 1 to which was added a large excess of free PEt3 showed only the unperturbed resonances of 1 together with those of free PEt3 and no new resonances in the diamagnetic region that could be attributable to the hypothetical 18-electron Cp’NbCl2(PEt3)3. This result rules out both the presence of a significant amount of 18-electron adduct in equilibrium with 1 and a rapid PEt3 exchange (on the NMR time scale) for compound 1.

**Table 5. Geometrical Parameters for MP2 Geometry-Optimized, 16-Electron CpNbCl2(PH3)2**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>exptl</th>
<th>calculated</th>
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<tbody>
<tr>
<td>Cp’NbCl2(PEt3)2</td>
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<tr>
<td>Nb–C(P) (av)/Å</td>
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<tr>
<td>Nb–Cl (av)/Å</td>
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<tr>
<td>Nb–P (av)/Å</td>
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<td>CI–Nb–P (av)/deg</td>
<td>81.7(7)</td>
<td>78.98</td>
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<td>CI–Nb–Cl (av)/deg</td>
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<td>P–Nb–P (av)/deg</td>
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<td>-294.9550</td>
<td>-294.9563</td>
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</table>

* Energies are in hartree units.

(a) Theoretical Calculations. The model system, CpNbCl2(PH3)2, was used for the theoretical calculations in both possible spin states, singlet or triplet. The calculations consisted of unrestricted open-shell SCF followed by a second-order Møller–Plesset (MP2) geometry optimization (see Experimental Section).

The optimized geometrical parameters are collected in Table 5. All of the geometric parameters for the $^3A'$ system compare extremely well with those experimentally found for 1, whereas the parameters optimized for the $^3A''$ system are quite different. This indicates that the experimentally determined singlet ground state for 1 in solution is also retained in the solid state. The $^3A''$ state shows, as expected, slightly longer Nb–ligand distances relative to the $^3A'$ state. The most interesting difference, however, is the variation of the CNT–Nb–Cl and CNT–Nb–P angles as a function of the spin state. The CNT–Nb–Cl angle closes from 124.28 to 112.13° upon going from the singlet to the triplet state, while the CNT–Nb–P angle correspondingly opens from 106.50 to 124.9°. This trend follows the experimentally determined angles in spin singlet and spin triplet systems (see Table 1) and can be attributed to the change of CI–Nb π-interactions, as previously discussed in the literature.2,3

The $^3A''$ state is calculated as the ground state at this level of theory, while the $^3A'$ state is 5.15 kcal/mol higher in energy or 6.02 kcal/mol when using the spin-projected wave function. The small difference between these two numbers is additional indication of the small spin contamination of the wave function from the unrestricted open-shell calculation (see Experimental Section). A single point calculation at the optimized geometry by including diffuse and polarization functions on the Cl and P atoms gave a smaller difference: the singlet state is now more stable than the triplet by 0.82 kcal, whereas the triplet is more stable by 0.25 kcal if the spin-projected wave function is used.

**Discussion**

The variable-temperature $^1$H-NMR experiments presented here establish a Curie–Weiss behavior for the previously reported15,16 spin triplet Cp’NbCl2(PMe3)2 compound. Conversely, compound 2 has a spin singlet ground state without appreciable population of a triplet excited state. Finally, compound 1 has an intermediate

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(40) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. Polyhedron 1987, 6, 705.
(41) Raner, K. CurveFit, version 0.7e; Clayton, Victoria, Australia, 1992.*
behavior, showing a thermal equilibrium between a ground state singlet and a thermally populated triplet. The variation of magnetic properties along the examined series of Nb(III) compounds deserved a detailed analysis. The choice of the ground state depends, in simple terms, on the competing effects of the pairing energy, PE, which favors a high spin arrangement, and the orbital splitting, which favors a spin-paired situation. The nature of the ligands could have an effect on either or both parameters.

The pairing energy is probably affected only by the electron-donating power of the phosphine and ring ligands, the better donor ligands expanding the metal orbitals and lowering PE. However, the electron-richest system, e.g. Cp*NbCl2(PMe3)2, is a pure paramagnet, whereas the opposite would be predicted by the pairing energy variation argument. A better correlation can be found on the basis of a variation of orbital splitting, which can be indirectly brought about by structural changes enforced by steric effects. As discussed in the literature,1–3 the M–Cl \( \pi \)-interaction diagram is as shown in Scheme 1. The major \( \pi \) interaction between the two Cl atoms and the metal is established between the metal \( d_{z^2} \) orbital and a symmetry-adapted linear combination of two Cl lone pairs, which has the effect of increasing the gap between the two frontier orbitals. The interaction is maximized at a CNT–M–Cl angle of 135°. A large steric interaction between the ring and the phosphine ligands forces the CNT–M–L angle to be large. This, in turn, induces a small CNT–M–Cl angle because of the \( \sigma \)-hybridization as detailed by Lin and Hall,1 ultimately reducing the \( \Delta \) gap and favoring higher spin configurations. This effect fully rationalizes the observed trend, the bulkier systems having a preference to be paramagnetic. This correlation is applicable only for systems where the X2L2 set of ligands adopts a relative trans configuration, for which the angular trans influence operates.2,3 Compound 2 presumably has a cis configuration [as established crystallographically for the similar CpMoBr2(dppe)].42 On the basis of this correlation, however, it is possible to predict that compounds such as CpNbCl2L2 with small phosphine ligands should be diamagnetic.

The results of the theoretical calculations (e.g. a more stable triplet state for the unencumbered CpNbCl2- (PH3)2 model complex) presented in this work must not be overinterpreted, since the two spin states experience a different degree of electronic correlation and this is only estimated as a second-order perturbation on the monoelectronic Hamiltonian by the MP2 calculation. However, the small calculated triplet–singlet gap of 5.15 kcal/mol (or \(-8.02\) kcal/mol with an expanded basis set on Cl and P) qualitatively agrees with the delicate balance of this system. The more positive result of the computational work is that the optimized geometries for both spin states follow the experimentally determined correlation of the CNT–M–X angles and the spin state for a 16-electron four-legged piano stool geometry.

As a final note, it is interesting to compare the magnetic properties of isoelectronic and isostructural four-legged piano stool Zr(II), Nb(III), and Mo(IV) systems. On one side, the Zr(II) systems6–9 are all diamagnetic and their structures show large CNT–Zr–X (X = halogen) angles. On the other side, all the Mo(IV) systems11,12 have a triplet ground state and their structures show small CNT–Mo–Cl angles (see Table 1). In between these two extremes, the Nb(III) systems examined in this work exhibit an intermediate behavior. This trend is consistent with the expected change of pairing energy (\( Zr^{2+} < Nb^{3+} < Mo^{4+} \)), correlating with variations of the effective nuclear charge along this series of isoelectronic 4d2 ions.

Conclusions

The synthesis of open-shell intermediate oxidation state organometallic niobium complexes has been accomplished by reduction of higher valent CpNb chlorides in the presence of phosphines. Within the general class of complexes, (ring)NbCl2L2 (L = tertiary phosphine), remarkably different magnetic properties can be found, ranging from pure spin triplet paramagnets to spin singlet/triplet equilibrium systems and finally to pure diamagnetic systems. The examples provided in this work, combined with isoelectronic systems of Zr(II) and Mo(IV), are consistent with the expected increase of pairing energies for higher oxidation states and reveal a correlation between the CNT–M–X angle (X = \( \pi \)-donor ligand) and the observed magnetic properties, with those complexes having large angles being diamagnetic. This is attributed to a better overlap of the donor lone pairs with the metal \( d_{z^2} \) orbital.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9508521) for support of this work.

Supporting Information Available: For compound 1, tables of crystal data and refinement parameters, fractional atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates (9 pages). Ordering information is given on any current masthead page.