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Synthesis and Properties of Cyclopentadienylniobium(III) Complexes. A Magneto–Structural Correlation for 16-Electron Four-Legged Piano Stool Complexes†

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Sodium reduction of (ring)NbCl₄ in the presence of the appropriate phosphine ligand affords the 16-electron Nb(III) complexes (ring)NbCl₂L₂ (ring = C₅H₅, L₂ = dppe or ring = C₅H₄Me, L = PET₃). While the previously reported Cp^{*}NbCl₂(PMe₃)₂ complex behaves as a Curie–Weiss spin triplet paramagnet, compound (C₅H₄Me)NbCl₂(PET₃)₂ has a spin singlet ground state and a thermally populated excited triplet state (2.3 kcal/mol higher in energy) and (C₅H₅)NbCl₂(dppe) is essentially diamagnetic. The X-ray structure of (C₅H₄Me)NbCl₂(PET₃)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 ¹A' and ³A'' states for the (C₅H₅)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 (d²) configuration, the four-legged piano stool structure has been verified crystallographically for compounds of group 4 metals in the oxidation state II, e.g. (η⁶-arene)M[(μ-X)₂AlX₂]₂ (M = Ti, Zr, Hf; X = Cl, Br, I)^{4,5} and (η⁶-arene)MX₂L₂ (arene = toluene; M = Zr, Hf; X = Cl, I; L = PMe₃),^{6–9} for the V(III) compound CpVCl₂(PMe₃)₂,¹⁰ and for a few Mo(IV) systems, e.g. [CpMoCl₂(PMe₃)₂]⁺ and Cp^{*}MoCl₃–(PR₃) (PR₃ = PMe₃, PMePh₂).^{11,12} The group 4 M(II) complexes are all diamagnetic, whereas the isoelectronic V(III) and Mo(IV) 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–M–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 d_{z²} 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(PMe₂–Ph)₂ with a magnetic susceptibility of 2.54 μ_B. 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 d⁰ complex [Cp^{*}WMe₄]⁺, would be unprecedented for a d² system.

† Dedicated to the memory of Sir Geoffrey Wilkinson.

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(1) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180–188.

(2) Poli, R. *Organometallics* **1990**, *9*, 1892–1900.

(3) Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 19–23.

(4) Calderazzo, F.; Pampaloni, G. *J. Organomet. Chem.* **1992**, *423*, 307–328.

(5) Calderazzo, F.; Pampaloni, G. *J. Organomet. Chem.* **1995**, *500*, 47–60.

(6) Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 908–909.

(7) Green, M. L. H.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1865–1867.

(8) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Walker, N. M.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 417–422.

(9) Diamond, G. M.; Green, M. L. H.; Walker, N. M.; Howard, J. A. K.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2641–2647.

(10) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193–204.

(11) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599–4607.

(12) Abugideiri, F.; Keogh, D. W.; Poli, R. *J. Chem. Soc., Chem. Commun.* **1994**, 2317–2318.

(13) Hessen, B.; Lemmen, T. H.; Luttikhedde, H. J. G.; Teuben, J. H.; Petersen, J. L.; Huffman, J. C.; Jagner, S.; Caulton, K. G. *Organometallics* **1987**, *6*, 2354–2362.

(14) Hessen, B.; Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H.; Helgesson, G.; Kakansson, M.; Jagner, S.; Spek, A. L. *Organometallics* **1993**, *12*, 2268–2276.

(15) Siemeling, U.; Gibson, V. C. *J. Organomet. Chem.* **1992**, *424*, 159–161.

(16) de la Mata, J.; Galakhov, M. V.; Gomez, M.; Royo, P. *Organometallics* **1993**, *12*, 1189–1192.

Table 1. Angular Parameters (deg) in Spin Singlet and Triplet 16-Electron Four-Legged Piano Stool Compounds of Type *trans*-(ring)MX₂L₂

compd	S	CNT–M–X	CNT–M–L	ref
(η^6 -toluene)ZrCl ₂ (PMe ₃) ₂	0	125.3(1)	109.4(1)	9
(η^6 -C ₇ H ₈)ZrCl ₂ (PMe ₃) ₂ ^a	0	130.1(1)	109.8(1)	8
(η^6 -C ₇ H ₇ SiMe ₃)ZrI ₂ (PMe ₃) ₂ ^b	0	127.9(1)	110.3(1)	6
CpVCl ₂ (PMe ₃) ₂	1	117.0(0)	113.7(0)	10
[CpMoCl ₂ (PMe ₃) ₂] ⁺	1	118.5(1)	113.2(1)	11
[Cp*MoCl ₂ (PMe ₂ Ph) ₂] ⁺	1	110.9(1)	121.6(1)	43

^a C₇H₈ = cycloheptatriene. ^b C₇H₇SiMe₃ = (trimethylsilyl)cycloheptatriene.

Table 2. NMR Data^a

complex	NMR ^a	
	¹ H (δ, ppm)	³¹ P (δ, ppm)
<i>T</i> = 290 K		
1	54.7 (b, <i>w</i> _{1/2} = 893 Hz, Cp')	
	2.20 (b, <i>w</i> _{1/2} = 56 Hz, PET ₃)	
	−21 (b, <i>w</i> _{1/2} = 7100 Hz, PET ₃)	
<i>T</i> = 283 K		
2	8.4–7.3 (m, 10 H, Ph ₂ P)	41.4 (s, dppe)
	6.6–5.5 (m, 10 H, Ph ₂ P)	
	5.87 (s, 5 H, Cp)	
	3.20 (bm, 2 H, PCH ₂ CH ₂)	
	2.95 (bm, 2 H, PCH ₂ CH ₂)	

^aThe 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(PET₃)₂ (Cp' = η^5 -C₅H₄Me) 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 conventional 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 spectrometers; the peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks (¹H) or downfield of external 85% H₃PO₄ (³¹P). For each ³¹P-NMR spectrum a sealed capillary containing H₃PO₄ was immersed in the same NMR solvent used for the measurement, and this was used as the reference. The elemental analyses were by M-H-W Laboratories, Phoenix, AZ, or Galbraith Laboratories, Inc., Knoxville, TN. Cp'NbCl₄,¹⁷ CpNbCl₄,¹⁷ and Cp*NbCl₂(PMe₃)₂^{15,16} were prepared by following the literature procedures. PMe₃ (Aldrich), PMe₂Ph (Aldrich), and dppe (Strem) were used as received. The NMR characterization data for all new compounds are given in Table 2.

Synthesis of Cp'NbCl₂(PET₃)₂ (1). Cp'NbCl₄ (1.031 g, 3.29 mmol) was added to a toluene solution (70 mL) of amalgamated Na (0.157 g, 6.83 mmol in 17 g of Hg) and PET₃ (0.970 mL, 6.57 mmol). After being stirred overnight, the resulting dark red-purple solution was evaporated to an oil; the residue was extracted with heptane (200 mL) and filtered through Celite. The resulting red-purple solution was placed at −80 °C for 2 h, and a red solid precipitated. The solid was filtered off and dried under reduced pressure. Yield: 0.936 g, 62%. Anal. Calcd for C₁₈H₃₇Cl₂NbP₂: C, 45.1; H, 7.8. Found: C, 44.9; H, 7.9. μ_{eff} = 1.09 μ_{B} (Evans' method in C₆D₆ at 277 K).

Table 3. Crystallographic Data for 1

formula	C ₁₈ H ₃₇ Cl ₂ NbP ₂
fw	479.23
cryst size (mm)	0.20 × 0.20 × 0.20
cryst system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	8.0735(5)
<i>b</i> , Å	13.9677(9)
<i>c</i> , Å	20.458(2)
β , deg	90.3421(7)
<i>V</i> , Å ³	2306.9(3)
<i>Z</i>	4
<i>D</i> _{calc} , g/cm ³	1.380
λ (Mo K α), Å	0.710 73
μ (Mo K α), mm ^{−1}	0.420
temp, K	293(2)
θ _{range} , deg	2.47–22.47
data collcd (<i>hkl</i>)	±8, −15, +22
no. reflns	3091
refinement method	full-matrix least-squares on <i>F</i> ²
data/restr/param	2995/0/215
GOF	1.038
<i>R</i> 1, %	4.98
<i>wR</i> 2, %	8.08

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–CNT ^a	2.018
Nb–P(1)	2.625(2)		
Cl(2)–Nb–Cl(1)	114.38(7)	P(1)–Nb–P(2)	148.96(7)
Cl(2)–Nb–P(1)	81.66(7)	Cl(1)–Nb–CNT ^a	116.9
Cl(1)–Nb–P(1)	82.45(6)	Cl(2)–Nb–CNT ^a	128.7
Cl(2)–Nb–P(2)	80.95(7)	P(1)–Nb–CNT ^a	104.6
Cl(1)–Nb–P(2)	81.61(7)	P(2)–Nb–CNT ^a	106.3

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

Synthesis of CpNbCl₂(dppe) (2). CpNbCl₄ (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 1/3 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. Calcd for C₃₁H₂₉Cl₂NbP₂: 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 $\omega/2\theta$ 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.¹⁸ 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 C¹⁹ and the relativistic ECP sets of Hay and Wadt for the heavier atoms.^{20–22} 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 C_s symmetry. The mean value of the spin of the first-order electron wave function, which is not an exact eigenstate of S² for unrestricted Hartree–Fock calculations on open-shell systems, was considered to identify unambiguously the spin state. The value of $\langle S^2 \rangle$ 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,^{23,24} supplemented with diffuse functions and 3 sets of d and 1 set of f polarization functions for the Cl and P atoms. The value of $\langle S^2 \rangle$ 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 = C₅H₄Me (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 phosphine; see eq 1. The products were isolated as crystalline materials and characterized by ¹H- and ³¹P-NMR spectroscopy and by elemental (C,H) analysis. Compound **1** was also characterized by X-ray crystallography.

ring = Cp', L = PEt₃; ring = Cp, L₂ = dppe

Half-sandwich compounds of Nb(III) with phosphine ligands that are already reported in the literature are either of the 18-electron type when the ligands are relatively unencumbering, e.g. CpNbCl₂(PMe₃)₃,²⁵ or of the 16-electron type for bulkier systems, e.g. Cp*NbCl₂L₂ (L = PMe₃,¹⁵ PMe₂Ph₂,¹⁶ and L₂ = dppe¹⁶). Compound **1** does not appear to lead to an 18-electron derivative when excess PEt₃ is added (see later); thus, the combination of the Cp' and PEt₃ ligands is already sufficient to prevent the achievement of a saturated structure. The

Figure 1. Side view (a) and top view (b) of **1**. Thermal ellipsoids are drawn at 40% probability level.

synthesis of other systems with intermediate steric crowding in the coordination sphere, e.g. (ring)-NbCl₂(PMe₂Ph)₂ (ring = Cp' and Cp), was attempted but only impure mixtures (presumably containing the 16-electron and 18-electron Nb(III) species and also Nb(IV) species of incomplete reduction, as shown by a combination of NMR and EPR spectroscopies) were obtained under a variety of different conditions, and the preparation of these systems was therefore abandoned.

As mentioned in the Introduction, 16-electron four-legged piano stool complexes can have one of two possible ground states of different spin, a singlet and a triplet. Preliminary NMR investigations for the isolated complexes indicate that compound **2** is diamagnetic, while compound **1** is paramagnetic with contact shifts comparable to those reported previously for Cp*NbCl₂L₂ (L = PMe₃,¹⁵ PMe₂Ph₂¹⁶ and L₂ = dppe¹⁶); see Table 2. Detailed variable-temperature NMR studies, however, reveal a more complex and interesting situation (*vide infra*).

X-ray structure of Cp'NbCl₂(PEt₃)₂. Two different ORTEP views of **1**, the first 16-electron CpNb^{III} complex to be crystallographically characterized, are shown in Figure 1. Selected bond lengths and angles are given in Table 4. The molecule exhibits a typical four-legged piano stool geometry, with an η⁵-bound Cp' ring and a relative trans configuration for the Cl₂(PEt₃)₂ set of ligands. The molecule is structurally identical to a well-studied and documented class of compounds of the form CpMoX₂L₂ (L = tertiary phosphine).²⁶ A comparison of the bond lengths and angles of this complex with the

(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.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94 (Revision A1)*; Gaussian Inc.: Pittsburgh, PA, 1995.

(19) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976; pp 1–28.

(20) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.

(21) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.

(22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.

(23) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(24) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(25) Alt, H. G.; Engelhardt, H. E. *Z. Naturforsch.* **1989**, *44b*, 367–368.

(26) Poli, R. *J. Coord. Chem. B* **1993**, *29*, 121–173.

recently described $\text{CpMoCl}_2(\text{PEt}_3)_2$ ²⁷ results in the observation of a lengthening 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 $\text{CpMoCl}_2(\text{PEt}_3)_2$. An 18-electron $\text{CpNb(III) isocyanide complex, Cp}^*\text{NbCl}_2(\text{CN-2,6-Me}_2\text{C}_6\text{H}_3)_3$, has also been crystallographically characterized, and a Nb–CNT bond length was found to be 2.099(5),²⁸ 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, $\text{Cp}^*\text{NbCl}_2(\text{CN-2,6-Me}_2\text{C}_6\text{H}_3)_3$, shows a significantly longer Nb–Cl bond, 2.561(2) Å.²⁸ All these trends may be explained on the basis of changes in M–Cl and M– PEt_3 π -bonding. The M– PEt_3 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 $\text{Cp}^*\text{NbCl}_2(\text{CN-2,6-Me}_2\text{C}_6\text{H}_3)_3$, there are no empty metal orbitals available for the establishment of a Nb–Cl π -interaction. Another interesting difference between the $\text{CpMCl}_2(\text{PEt}_3)_2$ (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 isoelectronic vanadium system, $\text{CpVCl}_2(\text{PMe}_3)_2$.¹⁰ 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 reported^{15,16} $\text{Cp}^*\text{NbCl}_2(\text{PMe}_3)_2$ were probed by variable-temperature ^1H -NMR studies. For compound $\text{Cp}^*\text{NbCl}_2(\text{PMe}_3)_2$, the contact-shifted resonances for both the Cp* and the PMe_3 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 ^{31}P -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

Figure 2. Plot of δ versus $1/T$ for $\text{Cp}^*\text{NbCl}_2(\text{PMe}_3)_2$.

the phosphorus atom due to the vicinity of the quadrupolar Nb nucleus ($I = 9/2$, 100% abundance, $Q = -0.366(18) \times 10^{-24} \text{ cm}^2$, vs $Q = -0.00282(19) \times 10^{-24} \text{ cm}^2$ for ^2H).²⁹ A possible slight population of a paramagnetic excited state is ruled out, since the position of the ^{31}P -NMR resonance does not shift upon further cooling to 213 K. Few diamagnetic Nb phosphine compounds appear to have been investigated by ^{31}P -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) MoCl_3L compounds: the Cp protons (e.g. for $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})$) are not observed in the ^1H -NMR spectrum, while the Cp* protons for $\text{Cp}^*\text{MoCl}_3(\text{PMe}_2\text{Ph})$ are observed at δ 0.6.³² The two additional resonances at δ –21 and 2.20 for **1** are tentatively assigned to the methylene and methyl protons of the PEt_3 ligand, respectively. Lowering the temperature, however, resulted in a shift of all resonances toward the diamagnetic region, contrary to the case of $\text{Cp}^*\text{NbCl}_2(\text{PMe}_3)_2$. 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}

$$\delta_{\text{obs}} = \delta_{\text{dia}} + \frac{g\beta H_0 A}{3kT(\gamma_{\text{H}}/2\pi)} \frac{6e^{-E/kT}}{1 + 3e^{-E/kT}} \quad (2)$$

The constants in eq 2 have their usual meanings, while δ_{dia} is the non-contact-shifted chemical shift, A is the hyperfine electronic coupling constant, and E is the

(27) Cole, A. A.; Fetting, J. C.; Keogh, D. W.; Poli, R. *Inorg. Chim. Acta* **1995**, *240*, 355–366.

(28) Alcade, M. I.; de la Mata, J.; Gomez, M.; Royo, P. *Organometallics* **1994**, *13*, 462–467.

(29) Raghavan, P. *At. Data Nucl. Data Tables* **1989**, *42*, 189–292.

(30) Schrock, R. R. *J. Organomet. Chem.* **1976**, *21*, 373–379.

(31) Jamieson, G.; Lindsell, W. E. *Inorg. Chim. Acta* **1978**, *28*, 113–118.

(32) Abugideiri, F.; Gordon, J. C.; Poli, R.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1575–1582.

(33) Kriley, C. E.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1994**, *116*, 5225–5232.

(34) Cotton, F. A.; Chen, H. C.; Daniels, L. M.; Feng, X. *J. Am. Chem. Soc.* **1992**, *114*, 8980–8982.

(35) Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915–4917.

Figure 3. Plots of δ versus T for the ^1H -NMR spectrum of **1**. Upper and lower plots correspond to the resonances assigned to the Cp' methyl protons and PET_3 methyl protons, respectively.

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 δ_{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, δ_{diag} , are 1(2) and 0.8(4) ppm, respectively, for the Cp' methyl and PET_3 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 PET_3 to a solution of compound **1** did not show any evidence for coordination with formation of a (diamagnetic) 18-electron compound: The ^1H -NMR spectrum of a solution of compound **1** to which was added a large excess of free PET_3 showed only the unperturbed resonances of **1** together with those of free PET_3 and no new resonances in the diamagnetic region that could be attributable to the hypothetical 18-electron $\text{Cp}'\text{NbCl}_2(\text{PET}_3)_3$. This result rules out both the presence of a significant amount of

Table 5. Geometrical Parameters for MP2 Geometry-Optimized, 16-Electron $\text{Cp}'\text{NbCl}_2(\text{PH}_3)_2$

	exptl $\text{Cp}'\text{NbCl}_2(\text{PET}_3)_2$	calculated $\text{Cp}'\text{NbCl}_2(\text{PH}_3)_2$	
		$^3\text{A}''$	$^1\text{A}'$
Nb–C(Cp)(av)/Å	2.343(7)	2.483	2.374
Nb–Cl (av)/Å	2.461(2)	2.575	2.537
Nb–P(av)/Å	2.631(2)	2.706	2.656
Cl–Nb–P(av)/deg	81.7(7)	78.98	80.87
Cl–Nb–Cl/deg	114.38(7)	135.73	111.14
P–Nb–P/deg	148.96(7)	119.02	146.97
CNT–Nb–Cl(av)/deg	122.8(1)	112.13	124.28
CNT–Nb–P(av)/deg	105.4(1)	120.49	106.50
$E(\text{LANL2DZ})^a$		–294.3316	–294.3234
$E(\text{LANL2DZ}/6\text{-}311\text{G})^a$		–294.9550	–294.9563

^a Energies are in hartree units.

18-electron adduct in equilibrium with **1** and a rapid PET_3 exchange (on the NMR time scale) for compound **1**.

Theoretical Calculations. The model system, $\text{Cp}'\text{NbCl}_2(\text{PH}_3)_2$, 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 $^1\text{A}'$ system compare extremely well with those experimentally found for **1**, whereas the parameters optimized for the $^3\text{A}''$ 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 $^3\text{A}''$ state shows, as expected, slightly longer Nb–ligand distances relative to the $^1\text{A}'$ 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 120.49°. 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 Cl–Nb π -interactions, as previously discussed in the literature.^{2,3}

The $^3\text{A}''$ state is calculated as the ground state at this level of theory, while the $^1\text{A}'$ 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 ^1H -NMR experiments presented here establish a Curie–Weiss behavior for the previously reported^{15,16} spin triplet $\text{Cp}^*\text{NbCl}_2(\text{PMe}_3)_2$ compound. Conversely, compound **2** has a spin singlet ground state without appreciable population of a triplet excited state. Finally, compound **1** has an intermediate

(36) Holm, R. H.; Hawkins, C. J. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(37) Boersma, A. D.; Phillipi, M. A.; Goff, H. M. *J. Magn. Reson.* **1984**, *57*, 197.

(38) Campbell, G. C.; Haw, J. F. *Inorg. Chem.* **1988**, *27*, 3706.

(39) Campbell, G. C.; Reibenspies, J. H.; Haw, J. F. *Inorg. Chem.* **1991**, *30*, 171.

(40) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705.

(41) Raner, K. *Curve Fit*, version 0.7e; Clayton, Victoria, Australia, 1992.

Scheme 1

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 π -interaction diagram is as shown in Scheme 1. The major π 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 σ -rehybridization as detailed by Lin and Hall,³ ultimately reducing the Δ 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 –0.82 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) systems^{6–9} are all diamagnetic and their structures show large CNT–Zr–X (X = halogen) angles. On the other side, all the Mo(IV) systems^{11,12} 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 (Zr²⁺ < Nb³⁺ < Mo⁴⁺), 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 = π -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.

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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.

(42) Krueger, S. T.; Owens, B. E.; Poli, R. *Inorg. Chem.* **1990**, *29*, 2001–2006.

(43) Abugideiri, F.; Keogh, D. W.; Kraatz, H.-B.; Poli, R.; Pearson, W. J. *Organomet. Chem.* **1995**, *488*, 29–38.