Table I. Determination of pK_a Values (Aqueous Scale Extrapolated from Nonaqueous Solvent Systems) by Use of $HPCy_3^+$ as a Standard (pK_a = 9.70) (BF_4^- Counterions, Except for $HPCy_3^+$ (BPh_4^-))

reactant				
$M'H_2^+$	MH	K_{eq}[a]	MH_2^+ product	pK_a of MH_2^+
$[CpRu(H)_2(PPh_3)_2]^+$	$MH_2(dppe)_2$[b]	>50[c]	$[MH(H_2)(dppe)_2]^+$	>10
$[CpRu(H)_2(PPh_3)_2]^+$	CpRuH(dppp)	1.34	$[CpRu(H)_2(dppp)]^+$	8.4
$HPCy_3^+$[d]	$CpRuH(PPh_3)_2$	0.038	$[CpRu(H)_2(PPh_3)_2]^+$	8.3
$[CpRu(H_2)(dppm)]^+$	CpRuH(dppe)	1.71	$[CpRuH_2(dppe)]^+$	7.3[e]
$[CpRu(H)_2(PPh_3)_2]^+$	CpRuH(dppm)	0.068	$[CpRu(H_2)(dppm)]^+$	7.1

[a] ±5% error in K_{eq}, pK_a. [b] M = Fe, Ru, Os. [c] Lower-bound estimate; too large to measure. [d] See eq 4 for this pK_a determination. [e] Likely to be pK_a of $[CpRu(H_2)(dppe)]^+$ form.

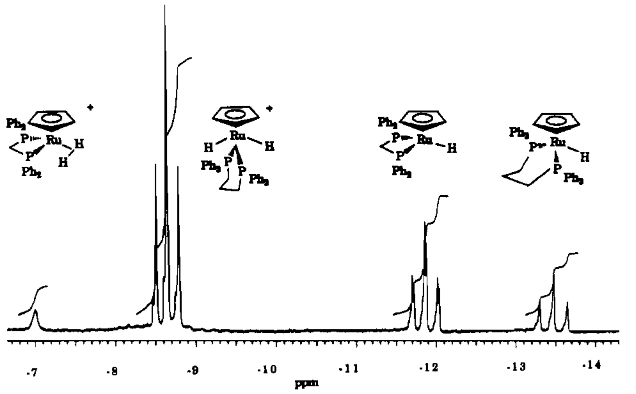


Figure 1. Hydride-region ^1H NMR spectrum (200 MHz) for the mixture of CpRuH(dppp) and $[CpRu(\eta^2\text{-}H_2)(dppm)]BF_4$ in CD_2Cl_2.

concentrations of the hydride complexes in solution and therefore the equilibrium constants (Table I).

The internal consistency of these equilibrium constants was confirmed by the fact that very similar values were obtained when the equilibrium was approached from the left or right side of eq 1. For example, for eq 2, an equilibrium constant of 18.4 was

$$[CpRu(H_2)(dppm)]^+ + CpRuH(dppp) \rightleftarrows CpRuH(dppm) + [CpRu(H)_2(dppp)]^+ \quad (2)$$

obtained if $[CpRu(\eta^2\text{-}H_2)(dppm)]BF_4$ and CpRuH(dppp) were mixed and 19.2 was obtained if CpRuH(dppm) and $[CpRu(H)_2(dppp)]PF_6$ were mixed. In addition, the equilibrium constant K_{eq3} for eq 3 is related to those of eq 2 and entry 2 of Table I:

$$[CpRu(H_2)(dppm)]^+ + CpRuH(PPh_3)_2 \rightleftarrows CpRuH(dppm) + [CpRu(H)_2(PPh_3)_2]^+ \quad (3)$$

i.e. $K_{eq3} = K_{eq2}/K_{entry2} = 18.8/1.34 = 14.0$. This is close to the experimentally determined value of 14.7 for K_{eq3}. Thus, the error in K_{eq} values by this method is less than 5%. The reaction of $[CpRu(H)_2(PPh_3)_2]^+$ with any of the complexes *cis*-$MH_2(dppe)_2$ went rapidly to completion so that only a lower bound on the pK_a of the complexes $[MH(H_2)(dppe)_2]^+$ has been obtained to date (see below). We were unable to rank the acidity of complexes $[MH(H_2)(dppe)_2]^+$ in dichloromethane by reaction with a dihydride $M'H_2(dppe)_2$ (M, M′ = Fe, Ru, Os) because reaction of the dihydride with CD_2Cl_2 was faster (minutes) than the proton-transfer reaction (hours).

To estimate the pK_a values of the ionic hydride complexes, we also determined the equilibrium constants for the reactions of $[CpRu(H)_2(PPh_3)_2]^+$ with PR_3 (R = Cy, *n*-Bu) (eq 4). The

$$[CpRu(H)_2(PPh_3)_2]^+ + PR_3 \rightleftarrows CpRuH(PPh_3)_2 + HPR_3^+ \quad (4)$$

aqueous pK_a values of $HPCy_3^+$ (9.70) and $HP(n\text{-}Bu)_3^+$ (8.43) have been previously determined by nonaqueous titrimetry in CH_3NO_2 and then extrapolated to the values for aqueous solution.[12] Compared with the case for the proton-transfer reactions, these phosphorus donor bases undergo substitution reactions at a negligible rate with the complexes $[CpRu(H)_2(PPh_3)_2]^+$ and $CpRuH(PPh_3)_2$. The equilibrium constant for eq 4 when R = Cy was 26, and the pK_a value for $[CpRu(H)_2(PPh_3)_2]^+$ was therefore calculated to be 8.3; for eq 4 when R = *n*-Bu, K_{eq} = 0.65, and hence pK_a($[CpRu(H)_2(PPh_3)_2]^+$) = 8.6. Thus, the two bases give values that fall within the error of the method (errors of peak integration, extrapolation of pK_a values between solvent systems, etc.). It should be noted that the pK_a values undergo approximately equal changes in relation to the values in H_2O (provided that no leveling occurs) for groups of chemically related substances.[13]

If we use $HPCy_3^+$ as a "standard", the pK_a values of the hydride complexes in aqueous solution should be close to the values shown in Table I.

Therefore, the acidity of the ionic hydride complexes can be ordered as $[CpRu(\eta^2\text{-}H_2)(dppm)]^+ > [CpRu(\eta^2\text{-}H_2)(dppe)]^+ \gg [CpRu(H)_2(PPh_3)_2]^+ > [CpRu(H)_2(dppp)]^+ \gg [MH(\eta^2\text{-}H_2)(dppe)_2]^+$. Thus, for similar types of complexes, the proton of the η^2-dihydrogen ligand is 1 order of magnitude more acidic than that of a hydride in an analogous complex (here it is assumed that the η^2-H_2 form of the dppe complex is responsible for its acidity). Note that the pK_a of the η^2-H_2 form of $[CpRu(H_2)(dmpe)]^+$ in CH_3CN was reported to be 17.6,[2] which translates into approximately 9.8 on the aqueous scale.[14] However, the ancillary ligands play an important role in determining the electron richness and hence the relative acidity of metal hydride complexes. Thus, the complexes $[MH(\eta^2\text{-}H_2)(dppe)_2]^+$ are more electron rich and less acidic than either the η^2-H_2 or $(H)_2$ forms of the cyclopentadienyl complex $[CpRuH_2(dppe)]^+$. The determination of the relative acidities of the complexes of the type $[MH(H_2)(L)_2]^+$ (M = Fe, Ru, Os; L = diphosphine) is in progress.

Acknowledgment. This research was supported by grants to R.H.M. from the Natural Sciences and Engineering Research Council of Canada and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a loan of ruthenium and osmium chlorides from Johnson-Matthey Co.

---

[12] Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

[13] Huber, W. *Titrations in nonaqueous solvents*; Academic Press: New York, 1967; p 11.

[14] On the basis of a pK_a for $HNEt_3^+$ of 18.46 in CH_3CN and 10.65 in H_2O. See: Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

Department of Chemistry and Scarborough Campus
University of Toronto
Toronto, Ontario, Canada M5S 1A1

Guochen Jia
Robert H. Morris*

Received September 11, 1989

A New Ortho-Metalated Dichloro-Bridged Complex of Iridium(III) with 2,2′-Bipyridine: $[\{Ir(bpy\text{-}C^3,N')(bpy\text{-}N,N')Cl\}_2][Cl]_2$

Combination of iridium chlorides with 2,2′-bipyridine under controlled conditions results in the formation of a novel ortho-metalated dichloro-bridged dimer. The product composition of

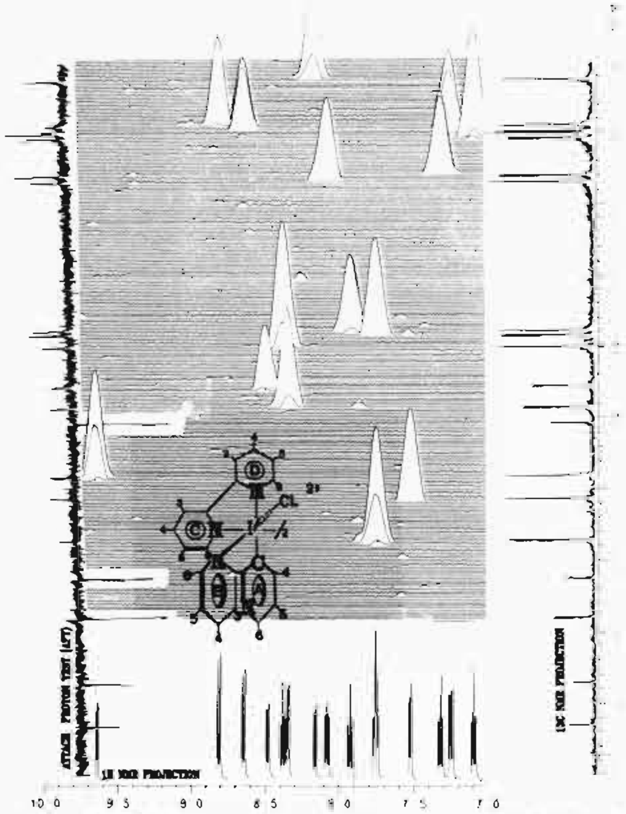


Figure 1. ^{1}H–^{13}C heteronuclear correlation spectrum (CSCM) of $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2]^{2+}$, with ^{1}H, ^{13}C, and APT NMR spectra projections.

$[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2]^{2+}$, is consistent with elemental, molecular weight, and mass spectroscopic analysis. The ^{1}H and ^{13}C NMR spectra give evidence for an ortho-metalated species with D_2 symmetry. Furthermore, this species possesses acid–base properties characteristic of a related bipyridine ortho-metalated complex, $[\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')_2]^{2+}$. While dichloro-bridged dimers of Ir(III) with traditional ortho-metalating ligands such as 2-phenylpyridine are common, the title complex represents the first report of a dichloro-bridged dimer of a bpy complex of Ir(III) and only the second instance of ortho-metalation of Ir(III) by bpy. The reaction conditions suggest that the presence of Ir(IV) promotes ortho-metalation by bpy, as would be anticipated in electrophilic substitution of a 3′-proton of bpy by the Ir(IV) electrophile.

Reaction of potassium hexachloroiridium(IV) (1.004 g, 2.08 mmol) and potassium hexachloroiridium(III) (1.004 g, 1.922 mmol) with 2,2′-bipyridine (2.001 g, 12.81 mmol) in 130 mL of 50% aqueous ethanol results in the formation of a complex with Ir, Cl, and bpy that was previously thought to be a *trans*-$[\mathrm{IrCl_2(bpy)_2}]^+$ species.[1] Although repeated recrystallization of the product does not afford ordered crystals suitable for X-ray analysis, the ^{1}H and ^{13}C NMR analysis of the product are indicative of either a *cis*-dichlorobis(2,2′-bipyridine)iridium(III) species or a dichloro-bridged dimer of Ir(III) with 2,2′-bipyridine. Elemental analysis, molecular weight determination,[2] and mass spectroscopy are consistent with a dimeric structure with a molecular composition $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2][\mathrm{Cl}]_2$. Furthermore, CV measurements show two reversible oxidation waves indicative of a dinuclear species.

The mass spectrum shows ion fragments with m/e 574 (12.2%), 539 (34.9%), 503 (4.6%), 185 (16.9%), and 157 (100.0%). The fragment at m/e 574 corresponds to the fragment $[\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')(\mathrm{Cl})_2]^+$, consistent with a heterolytic cleavage of the dimer. The m/e 539 and 503 fragments correspond to $[\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}]^+$ and $[\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')]^+$ respectively. Finally, the m/e 157 and 185 fragments correspond to the protonated free bipyridine ligand (bpy + $\mathrm{H^+}$) and bipyridine + $\mathrm{C_2H_5^+}$ (m/e 156 + 29)[3] respectively. These results were obtained with an ionization voltage of 2.2 eV, under desorption chemical ionization conditions. A lower ionization voltage, I = 14 mV, was utilized in order to detect ion fragments above m/e 1000. An ion fragment centered at m/e 1078 was detected which corresponds to the intact ortho-metalated dichloro-bridged Ir(III) dimer, $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2]^+$. More importantly, however, a strong m/e distribution of signals around m/e 1113 was observed which corresponds to an ion fragment with molecular formula $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2\mathrm{Cl}]^+$. The isotope cluster abundance calculation for $\mathrm{Ir_2C_{40}H_{30}N_8Cl_3}$ is consistent with the distribution at m/e 1113.

The ^{1}H–^{13}C heteronuclear correlation (CSCM) spectrum, Figure 1, shows the ^{1}H NMR spectrum between 10.0 and 7.0 ppm, integrating for 15 protons. These resonances correspond to a "three"-, "four"-, "four"-, and "four"-spin system in the homonuclear 2D COSY spectrum. The three spin system is interpreted as the ortho-metalated pyridyl ring of bipyridine. The ^{13}C and attached proton test (APT) NMR spectra, Figure 1, are consistent with the ^{1}H NMR spectrum, showing 15 protonated and 5 nonprotonated carbon resonances; the 15 protonated carbon resonances may be mapped to their appropriate proton resonances from the $J_{\mathrm{C-H}}$ coupling (peaks) in the CSCM spectrum. The quaternary carbon at 144.7 ppm is characteristic of a resonance of carbon bound to iridium, this resonance is assigned to the $\mathrm{A_3}$ carbon.[4] Nuclear Overhauser enhancement (NOE) ^{1}H difference spectra and the ^{1}H 2D COSY spectrum suggest that the Ir–C bonds are positioned in an axial position across Ir–N bonds, cis to the bridging chlorides.

The $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2]^{2+}$ dimer possesses acid–base photophysical properties characteristic of a related monomeric complex, $[\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N)(\mathrm{bpy}\text{-}N,N')_2]^{2+}$.[4-6] Absorption spectra were obtained in neutral (ethanol–methanol 1:1 v/v), acidic (ethanol–methanol 1:1 v/v and 0.01 M HCl) and basic (ethanol–methanol 1:1 v/v and 0.01 M NaOH) solvent systems. The absorption bands between 480 and 220 nm show a reversible acid–base dependence. Likewise, the emissions under neutral, acid, and base conditions at ambient and 77 K temperatures show acid–base dependence. At 77 K, the emission maxima at $\lambda_{\max}$ = 589–673 nm in basic solution blue shift to $\lambda_{\max}$ = 535–558 nm in acidic solution. The ambient temperature behavior shows a red shift from basic $\lambda_{\max}$ = 589 nm to acidic $\lambda_{\max}$ = 601 nm conditions. The acid–base character shown for this iridium complex is consistent with a species possessing a basic nitrogen site (as in the related monomeric complex). The proposed structure is consistent with this property.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (Contract DE-FG03-88ER13842).

Registry No. bpy, 366-18-7; $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2][\mathrm{Cl}]_2$, 123902-61-4; potassium hexachloroiridate(IV), 16920-56-2; potassium hexachloroiridate(III), 14024-41-0.

Supplementary Material Available: Figures illustrating the acid/base dependence of the ultraviolet–visible absorption spectrum and the 77 K emission spectrum of $[\{\mathrm{Ir}(\mathrm{bpy}\text{-}C^3,N')(\mathrm{bpy}\text{-}N,N')\mathrm{Cl}\}_2]\mathrm{Cl}_2$ (Figures S1 and

---

(1) Gillard, R. D.; Heaton, B. T. *Chem. Commun.* **1968**, 75.

(2) Anal. Calcd for $\mathrm{Ir_2C_{40}H_{30}N_8Cl_4\cdot 3(H_2O)}$: C, 39.94; H, 3.02; N, 9.31; mol wt, 1203. Found: C, 39.99; H, 3.15; N, 9.09; mol wt, 1228.

(3) $\mathrm{C_2H_5^+}$ is formed in high concentrations when $\mathrm{CH_4}$ is used as the carrier reagent gas under chemical ionization conditions.

(4) Spellane, P. J.; Watts, R. J.; Curtis, C. J. *Inorg. Chem.* **1983**, *22*, 4060. The resonance of ^{13}C bound to Ir(III) in $[\mathrm{Ir}(\mathrm{Hbpy}\text{-}C^3,N)(\mathrm{bpy}\text{-}N,N')_2]^+$ was found at 139.5 ppm.

(5) Wickramasinghe, W. A.; Bird, P. H.; Serpone, N. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1284.

(6) Nord, G.; Hazell, A. C.; Hazell, R. G.; Farver, O. *Inorg. Chem.* **1983**, *22*, 3429.

S2) (2 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of California
Santa Barbara, California 93106

Fred O. Garces
Richard J. Watts*

Received February 16, 1989

Soluble Niobium Polysulfide Complexes from the Reaction of (t-BuC$_5$H$_4$)$_2$NbH$_3$, (C$_5$Me$_5$)$_2$NbBH$_4$, and (C$_5$Me$_5$)Nb(CO)$_4$ with Sulfur

Transition-metal complexes with polysulfide ligands are of considerable interest because of their structural variety and their reactivity. Modern aspects of application include catalysis and materials science.[1] In this regard it is striking that only few soluble niobium polysulfide complexes have been reported although polyselenide chemistry of Nb is already well established.[1,2] With the only exception of $[Nb_2(OMe)_2(S_2)_3(S_5)O]^{2-}$,[3] known molecular niobium sulfides contain mono- or diatomic sulfur ligands together with one or two cyclopentadienyl ligands per Nb atom.[4] Here we report on a promising entry to niobium polysulfide chemistry by means of substituted niobium cyclopentadienides, e.g. Cp'_2NbH_3[5] ($Cp' = \eta^5$-t-BuC$_5$H$_4$), $Cp^*_2NbBH_4$[6] ($Cp^* = \eta^5$-C$_5$Me$_5$), or $Cp^*Nb(CO)_4$.[7] In their reactions with elemental sulfur the influence of steric and electronic factors on the nature of the products was studied.

Stirring of a toluene solution (18 h, 20 °C) of Cp'_2NbH_3 (or Cp'_2NbBH_4) with $^5/_8$ S_8 results in the instantaneous evolution of H_2S. After chromatographic workup on SiO_2 (5:1 toluene/ether), a mixture of two apparently very similar products was isolated.[8] Elemental analyses of this mixture were in agreement with a ratio 4:2:8 (or 9) for Cp′/Nb/S, although FD-mass spectra exhibited a considerably lower mass peak. This observation is indicative of a facile loss of Cp′ and sulfur ligands from **1** under thermal conditions.

Red-orange crystals of **1** were isolated by fractional crystallization from 2:1 toluene/pentane. An X-ray diffraction analysis[9] of these crystals shows as the principal result two $Cp'_2Nb(\eta^2$-$S_2)$ moieties linked together by a twisted pentasulfide chain (Figure 1). Inspite of the low quality of the structural solution (some of the Cp′ carbon atoms could not be localized) the core of the molecule could be determined unambiguously. The sulfide chain is one of the few examples in which polysulfide bridges do not form cyclic structures,[1,2] which may be responsible for the kinetic lability of **1**. This is expressed by the high thermal sensitivity in the mass spectrum as well as by the easy formation of niobium polysulfide compounds of higher nuclearity.[10] In this context it must be noted that there is spectroscopic evidence for dismutation reactions in solution for the structurally analogous μ-η^1-Se_5^{2-} ligand in $[Ph_4P]_4[In_2Se_{21}]$.[11] The existence of two different conformations may be explained by packing effects. Rotational isomers could not be detected in solution by ^{1}H NMR spectroscopy even after cooling a sample to −80 °C. This is in agreement with the generally low activation barrier for the rotation around the MCp bond in metallocenes.[12]

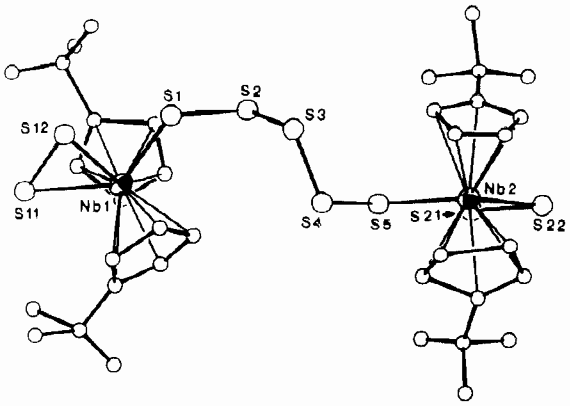
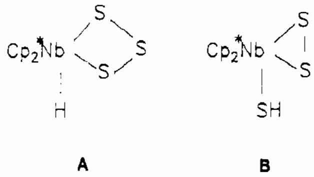


Figure 1. Structure of (t-BuC$_5$H$_4$)$_4$Nb$_2$S$_9$. Bond distances (Å): Nb(1)–S(1), 2.523 (6); Nb(1)–S(11), 2.462 (5); Nb(1)–S(12), 2.543 (8); Nb(2)–S(5), 2.524 (6); Nb(2)–S(21), 2.455 (6); Nb(2)–S(22), 2.514 (6); S(1)–S(2), 2.054 (9); S(2)–S(3), 2.111 (9); S(3)–S(4), 2.027 (9); S(4)–S(5), 2.056 (9); S(11)–S(12), 2.054 (9); S(21)–S(22), 2.01 (1). Bond angles (deg): S(1)–Nb(1)–S(12), 67.9 (2); S(11)–Nb(1)–S(12), 48.4 (2); S(5)–Nb(2)–S(21), 69.3 (2); S(21)–Nb(2)–S(22), 47.7 (2); $Cp(1)_{cent}$–Nb(1)–$Cp(2)_{cent}$, 128.7 (1); $Cp(3)_{cent}$–Nb(2)–$Cp(4)_{cent}$, 131.4 (1).

Variation of the substituents at the Cp ligands exerts a drastic influence on the nature of the products as shown in the reaction of $Cp^*_2NbBH_4$ with $^1/_2$ S_8 (THF, 20 °C, 60 min). After chromatographic workup on SiO_2 (toluene), two red orange compounds **2** and **3** were isolated. For complex **3**[13] (23% yield) the composition $Cp^*_2NbS_3H$ follows unambiguously from analytical and mass spectroscopic data. However, spectroscopic data and reactivity arguments do not yet allow one to differentiate between the two isomeric forms **A** and **B**. The presence of a ^{1}H NMR signal at $\delta = -1.64$ may be indicative of a hydrogen atom directly attached to the metal center, but it may be also representative of an SH proton. An argument supporting structure **2A** is the absence of any ν_{SH} absorption at about 2400 cm^{-1} in the IR



2

---

(1) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

(2) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. Schreiner, S.; Aleandri, L. E.; Kang, D.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 393.

(3) Müller, A.; Schimanski, J.; Römer, M.; Bögge, H.; Baumann, F.-W.; Eltzner, W.; Krickemeyer, E.; Billerbeck, U. *Chimia* **1985**, *39*, 25.

(4) Cp_2NbS_2Cl: Treichel, P. M.; Werber, G. P. *J. Am. Chem. Soc.* **1968**, *90*, 1753. Cp_2NbS_2Me: Amaudrut, J.; Guerchais, J. E.; Sala-Pala, J. *J. Organomet. Chem.* **1978**, *157*, C10. $Cp_4Nb_2S_2$: Skripkin, Y. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Y. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285. $[CpNb(CO)_2]_2(\mu$-$S)_n$ (n = 2, 3): Herrmann, W. A.; Biersack, H.; Ziegler, M. L.; Balbach, B. *J. Organomet. Chem.* **1981**, *206*, C33.

(5) Labinger, J. A. *Adv. Chem. Ser.* **1978**, *No. 167*, 149.

(6) Bell, R. A.; Cohen, S. A.; Doherty, N. M.; Threlkel, R. S.; Bercaw, J. E. *Organometallics* **1986**, *5*, 972.

(7) Herrmann, W. A.; Kalcher, W.; Biersack, H.; Bernal, I.; Creswick, M. *Chem. Ber.* **1981**, *114*, 3558.

(8) Compound **1** was analyzed correctly for C, H, and S. ^{1}H NMR (toluene-d_8, 24 °C): δ 6.19 (m, 4 H), 5.90 (m, 4 H), 5.59 (m, 4 H), 5.26 (m, 4 H), 1.17 (s, 36 H). IR (KBr): ν(S–S) 542 (m), 461 cm^{-1} (w). FDMS (m/z): 588 (mass accounts for $Cp'_2Nb_2S_5$). The second yet unidentified component in the mixture exhibits ^{1}H NMR data quite close to those of **1**. The yield is ca. 80% with respect to composition **1**.

(9) Crystal data for $C_{36}H_{52}Nb_2S_9$ (**1**): $P2_1/c$, a = 15.553 (1) Å, b = 10.339 (1) Å, c = 31.984 (3) Å, β = 92.9 (1)°, V = 5136.47 Å^3, Z = 4, μ(Cu) = 7.26 cm^{-1}, D(calcd) = 1.24 g·cm^{-3}; crystal, 90 × 150 × 180 μm; Enraf-Nonius CAD4 ($2 \le \theta \le 47°$), 5865 observed data ($I > 2\sigma(I)$, 4592 independent data, R(int) = 0.06. The metal atoms were located by using MULTAN. The other atoms were derived from difference Fourier syntheses. Of the 36 C atoms, 9 tended to drift from their positions. Fixing them resulted in acceptable bond angles and distances. Disorder problems could be excluded. R = 0.162 (Nb and S anisotropic).

(10) Warming solutions of **1** gives rise to the formation of (among others) the highly asymmetric cluster $Cp'_3Nb_3S_{12}$, which is distinguished by five different sets of S_n^{2-} ligands, n ranging from 1 to 3: Brunner, H.; Meier, W.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.*, in press.

(11) Kanatzidis, M. G.; Dhingra, S. *Inorg. Chem.* **1989**, *28*, 2026.

(12) Erker, G.; Nolte, R.; Tainturier, G.; Rheingold, A. *Organometallics* **1989**, *8*, 454. Erker, G.; Nolte, R.; Krüger, C.; Schlund, R.; Benn, R.; Grondey, H.; Mynott, R. *J. Organomet. Chem* .**1989**, *364*, 119.

(13) Compounds **2–4** all give correct elemental analyses (C, H, S.) ^{1}H NMR (CDCl$_3$, 24 °C): **2**, δ 1.78 (s, 30), −1.64 (s, 1); **3**, δ 1.83 (s); **4**, δ 2.20 (s, 30), 2.03 (s, 15). IR (KBr; cm^{-1}): **2**, ν(S–S) 543 s, ν(Nb–S) 354 (s), 323 (s); **3**, ν(S–S) 528 (m).

0020-1669/90/1329-0584$02.50/0