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Niobium−Mercury Heterometallic Compounds as Sources of Niobium(II): Radical Paths to Organoniobium Species

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The niobium−mercury compounds $[Cp'_2Nb(L)]_2Hg$ ($Cp' = \eta^5$-$C_5H_4SiMe_3$, L = CO (**4**), PMe_3 (**5**), or CN^tBu (**6**)) serve as stable precursors to the short-lived Nb(II) radicals of general formula $[Cp'_2Nb-L]$. The homolysis of the Nb−Hg bond may result from a slow thermal reaction (generating low concentrations of radicals) or from a photochemical process in which mercury extrusion is more rapid. Since the Nb(II) species show no evidence for Nb−Nb bond formation, they are useful in the synthesis of a variety of Nb(III) and Nb(IV) species. Reactions of **4** with dimeric species such as $[CpFe(CO)_2]_2$, $[CpNi(CO)]_2$, $Co_2(CO)_8$, or RSe−SeR give rise to new Nb−M or Nb−Se compounds, while reactions with potential π donors such as formaldehyde or azobenzene lead to displacement of the ligand L and formation of the Nb(IV) complexes. Crystallographic and variable-temperature NMR studies on the Nb−Fe compound $Cp'_2Nb(\mu$-$CO)_2Fe(CO)Cp$ (**10**) are consistent with a low-energy fluxional process involving exchange of bridging and terminal carbonyl ligands.

Introduction

It is widely recognized that transition-metal-centered radicals afford ample opportunity for the development of new chemistry of interest in synthesis and catalysis.[2] The majority of these radicals exhibit a 17-electron configuration and are known to be susceptible to one-electron processes, two-electron processes, or both. These reactions include substitution or atom transfer reactions yielding new metal−ligand bonds,[3] as well as reduction or oxidation reactions; oxidation usually involves prior addition of a ligand to form a 19-electron radical.[4] As expected, the susceptibility of the odd-electron species to both oxidation and reduction also makes them useful in disproportionation reactions; these may proceed as in eq 1 ($L_nM = CpMo(CO)_3$), with

$$\underset{17\ e^-}{L_nM^\bullet} \xrightarrow{L'} \underset{19\ e^-}{\left[L_nL'M^\bullet\right]} \xrightarrow[e^-\text{ transfer}]{L_nM\text{-}ML_n} \underset{18\ e^-}{L_nL'M^{\oplus}} + \underset{18\ e^-}{L_nM^{\ominus}} + \underset{17\ e^-}{L_nM^\bullet} \tag{1}$$

addition of L′ to give the 19-electron reductant. The net result is the production of two 18-electron species and a radical center to function as chain carrier. Many 17-electron species are also activated toward ligand substitution reactions, and the disproportionation mechanism (eq 1) illustrates the fact that associative pathways are available; the kinetic enhancement (relative to similar processes for diamagnetic analogues) is due to the availability of the 19-electron intermediates and associative reaction pathways that are not accessible to saturated diamagnetic compounds.[3c−f] For these reasons, the production of radical species is of considerable interest and a common synthetic approach involves photolytic homolysis of metal−metal bonds.[5] Clearly, however, the recombination of the resulting radicals often represents an undesirable outcome, one which may preclude the use of the radicals in synthetic applications. Indeed, a wide range of radical combination reactions have been the subject of quantitative study, and they exhibit second-order rate constants in the range 10^7−10^9 M^{-1} s^{-1}.[5,6] One approach used to circumvent simple coupling reactions involves the incorporation of large ligands into the coordination sphere;[7] this serves to slow dimerization but can also diminish the reactivity toward other substrates too. Hence, the goal is to develop radical-based systems that are easily accessible, exhibit substantial reactivity toward a variety of substrates, and are resistant to dimerization reactions. Clearly, these latter two criteria are often

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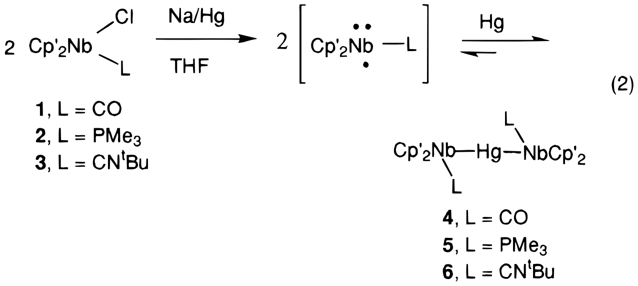
at odds, and useful systems must exhibit a fine balance between high reactivity and stability toward dimerization.

We have recently communicated our discovery of a series of heterometallic niobium−mercury compounds with a $L_nNb-Hg-NbL_n$ structure pattern.[8] These compounds (**4**−**6**) were isolated from the reduction of Nb(III)−halide precursors with sodium amalgam, and were proposed to arise from the attack of intermediate niobium(II) radicals on elemental mercury (eq 2, Cp′ = η^5-$C_5H_4SiMe_3$). The method involves synthesis of d^3 radicals, and if Nb−Hg bond formation is reversible, the heterometallic Nb−Hg product has the potential to serve as a convenient precursor for radical intermediates. Herein, we show that this is indeed the case and that the radicals may be generated using either thermal or photochemical stimulation; as such, the stable Nb−Hg compounds **4**−**6** constitute a convenient means of storing the Nb(II) radicals. These are susceptible to both one-electron and two-electron processes; the former generate niobium products with either (a) new niobium−ligand or (b) new niobium−metal bonds, while the latter provide access to ligand substitution reactions and products that are best formulated as niobium(IV) radicals. While the one-electron processes yield heterobimetallic compounds containing niobium and either middle or late transition metals, there is *no* evidence for dimerization of the niobium radicals.



Experimental Section

General Considerations. All manipulations involving metal complexes were carried out under an atmosphere of nitrogen which was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques were used to handle solutions,[9] and solids were transferred in a Vacuum Atmospheres Corp. glovebox under purified nitrogen. Elemental analysis (C, H) were performed by the Oneida Research Services, Inc., New York. Solvents toluene, hexane, and tetrahydrofuran (J. T. Baker) were distilled from sodium benzophenone ketyl under nitrogen. $NbCl_5$, $[Cp_2Fe_2(CO)_4]$, $Co_2(CO)_8$, and $[CpNi(CO)]_2$ (Aldrich) were commercial materials and used as supplied. Compounds **4**−**6** were prepared using literature methods.[8]

NMR spectra were obtained on a Varian Gemini 300 FT-NMR instrument, infrared spectra on a Perkin-Elmer model 1600 FT-IR spectrophotometer, ESR spectra on a Bruker ESP300 spectrometer, and voltammetric data with an EG&G VersaStat potentiostat interfaced to a 486 PC. The electrolytic cell was evacuated on a Schlenk line and then loaded with a solution of 0.5 M NBu_4PF_6 in THF. The reference electrode was prepared by inserting a short (ca. 1/4 in.) length of 5 mm porous vycor into a Teflon tube. The latter was filled with 0.1 M $AgNO_3/CH_3CN$ solution, into which a 16 gauge silver wire was immersed. The electrolytic solution was maintained under a nitrogen atmosphere by passing THF-saturated nitrogen through the cell. Photochemical experiments were carried out with a medium-pressure mercury lamp using Pyrex glassware; under these conditions, the principal photolysis wavelengths used are 313 and 365 nm.

Synthesis of $Cp'_2Nb(CO)(SePh)$ (9). $[Cp'_2Nb(CO)]_2Hg$ (**4**, 0.100 g, 0.100 mmol) and Ph_2Se_2 (31 mg, 0.1 mmol) were weighed into a gas inlet flask. Benzene (20 mL) was added, and the resulting solution was stirred at ambient temperature for ca. 15 min. NMR indicated that the reaction was quantitative, and the solvent was removed in vacuo to yield green **9**. ^1H NMR (C_6D_6): 5.39 (br s, 2H, Cp′), 4.92 (br s, 2H, Cp′), 4.71 (br s, 4H, Cp′), 0.19 (s, 18H, SiMe). ^{77}Se NMR (C_6D_6): −44.5. IR(benzene): 1926 (s), 1251 (m), 1096 (w), 1022 (w), 839 (m), 812 cm^{-1} (s).

Synthesis of $[Cp'_2Nb(\mu\text{-}CO)_2Fe(CO)Cp]$ (10). A solution of $[Cp'_2Nb(CO)]_2Hg$ (**4**) (0.23 g, 0.255 mmol) and $[FeCp(CO)_2]_2$ (0.09 g, 0.255 mmol) in 25 mL of toluene was irradiated under nitrogen for 45 min using a 450 W Hanovia medium-pressure mercury lamp. The resulting purple solution was filtered to remove mercury; concentration of this solution followed by addition of excess hexanes led to the precipitation of a purple solid, which was collected by filtration and dried *in vacuo* (0.18 g, 67%). ^1H NMR (C_6D_6): 4.87, 4.21 (4H each, br s, Cp′−H), 4.38 (5H, s, Cp), 0.28 (18H, s, SiMe). ^{13}C NMR (C_6D_6): 100.5, 99.1, 98.9 (Cp′), 90.98 (Cp), 0.00 (SiMe). IR (Nujol): 1909 (vs, CO), 1698 (vs,CO), 1243 (s), 1168 (s), 902.7, 839.7 cm^{-1}. Anal. Calcd for $C_{24}H_{31}FeNbO_3Si_2$: C, 50.35; H, 5.45. Found: C, 50.50; H, 5.52. Compound **11** was prepared similarly from **4** and equimolar $Co_2(CO)_8$. ^1H NMR (C_6D_6): 5.07 (br s, 4H, Cp′), 4.59 (br s, 4H, Cp′), 0.02 (s, 18H, SiMe). IR (benzene): 2029 (s), 1966 (s), 1949 (s), 1906 (m), 1251 (m), 838 cm^{-1} (m). Green **12** was prepared similarly from **4** and 1.5 equiv of $[CpNi(\mu\text{-}CO)]_2$; the reaction was photolyzed until IR indicated consumption of **4** (ca. 30−40 min), and **12** was isolated as a brown solid by precipitation from cold hexane. ^1H NMR (C_6D_6): 5.33 (s, 5H, Cp), 4.90 (br s, 4H, Cp′), 4.23 (br s, 4H, Cp′), 0.18 (s, 18H, SiMe). IR (benzene): 1745 (s), 1260 (m), 1164 (w), 1013 (m), and 838 cm^{-1} (s).

Synthesis of $Cp'_2Nb(\eta^2\text{-}PhNNPh)$ (13). $[Cp'_2Nb(CO)]_2Hg$ (**4**, 0.100 g, 0.100 mmol) and Ph_2N_2 (36 mg, 0.2 mmol) were weighed into a Pyrex tube with a gas inlet side arm. Benzene (ca. 20 mL) was added, and the resulting solution was irradiated (450 W mercury lamp) for ca. 45 min. NMR data were used to verify the loss of diamagnetic starting materials, and the solvent was removed in vacuo to yield green **13**. ESR (C_6H_6): $g = 1.9888$, $\langle a \rangle_{Nb} = 10$ G. IR (C_6H_6): 1588 (m), 1474 (m), 1248 (m), 902 (m), 839 (s), 803 (m), and 752 (s) cm^{-1}.

Crystal Structure Determination of 10. Compound **10** was crystallized by slowly cooling a hexanes solution to 0 °C, resulting in dark violet needles. A small, well-formed crystal measuring 0.60 × 0.09 × 0.09 mm was attached to a glass fiber and mounted on the Siemens SMART system for a data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 50 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced orientation matrices determined from 510 reflections.

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Table 1. Crystal Data for 10

empirical formula	$C_{24}H_{31}FeNbO_3Si_2$
fw	572.43
cryst habit	violet-brown needles
cryst size	0 .60 × 0.09 × 0.09 mm
space group	$P3_2$
temperature	173(2) K
a 12.0587(1) Å	
b 12.0587 (1) Å	
c 15.3204(3) Å	
volume	1929.31(4) Å^3
Z (molecules/cell)	3
density (calcd)	1.478 mg/m^3
abs coeff	1.125 mm^{-1}
R indices	R1 = 0.0292, wR2 = 0.0709
α	90°
β	90°
γ	120°

Table 2. Bond Lengths (Å) and Angles (deg) for 10

Nb(1)−Fe(1)	2.8156(6)
Nb(1)−C(1)	2.183(4)
Nb(1)−C(2)	2.184(4)
Fe(1)−C(1)	1.969(4)
Fe(1)−C(2)	1.997(4)
C(1)−O(1)	1.190(5)
C(2)−O(2)	1.188(5)
Fe(1)−C(3)	1.748(4)
C(3)−O(3)	1.159(5)
Nb(1)−C(1)−O(1)	144.1(3)
Nb(1) C(2)−O(2)	144.4(3)
Fe(1)−C(1)−O(1)	130.6(3)
Fe(1)−C(2)−O(2)	131.0(3)
C(1)−Nb(1)−Fe(1)	44.17(9)
C(1)−Fe(1)−Nb(1)	50.59(11)
C(2)−Nb(1)−Fe(1)	44.92(11)
C(2)−Fe(1)−Nb(1)	50.53(11)
Nb(1)−C(1)−Fe(1)	85.24(14)
Nb(1) −C(2)−Fe(1)	84.5(2)

Final cell constants were calculated from a set of 8192 strong reflections from the actual data collection. The space group $P3_2$ was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated, which provided most non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. Data are collected in Tables 1 and 2.

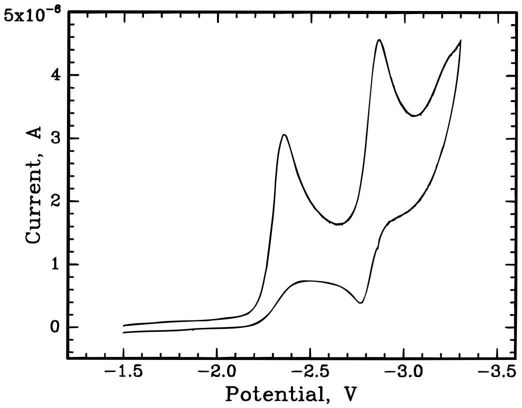

Figure 1. Cyclic voltammograms for **1**, 1 mM in THF with 1.0 M NBu_4PF_6. The working electrode is a platinum disk, the counter electrode a platinum wire, and the reference electrode is Ag/$AgNO_3$.

Results

Voltammetric Studies of Nb(III) Precursors. For niobocene compounds, Nb(III) is the lowest oxidation state commonly observed. A number of compounds of general formula $Cp'_2Nb(Cl)(L)$ (L = two-electron donor ligand) are available from the known $[Cp'_2Nb(\mu\text{-}Cl)]_2$, and these clearly contain an electron-rich Nb(III) center; many are prone to facile aerobic oxidation.[10] Nonetheless, we have used reduction reactions in a variety of synthetic processes which may proceed through Nb(II) intermediates and chose to undertake a synthetic and voltammetric study of this process. This led to the production of the niobium−mercury compounds shown in eq 2, and the details of the syntheses have already been published.[8] As such, we will devote this section to a description of the voltammetric experiments, the results of which are depicted in Figure 1. This contains the voltammogram obtained with 1 mM $Cp'_2Nb(Cl)(CO)$ (**1**) in THF solution; use was made of a platinum disk electrode and Ag/$AgNO_3$ reference electrode, and the potentials are related to that couple. It is clear that there are two one-electron processes operating here. The first of these is wholly irreversible at scan rates up to 500 mV s^{-1}, and this remains true even if the scan is reversed immediately after this first wave. This is commonly observed for this class of compounds,[11] and we attribute the irreversible nature of the reduction to the rapid loss of chloride. The second wave is quasi-reversible and is presumably due to conversion of the Nb(II) radical to the Nb(I) anion. The reduction of the 17-electron Nb(II) radical would give rise to an 18-electron anion and should not lead to loss of any ligand. Moreover, we see no evidence for production of this anion in the synthetic studies using sodium amalgam, which does not have sufficient reducing power to effect this second redox process. As a result, we have suggested that the production of the heterometallic compounds **4**−**6** is due to attack of the Nb(II) radicals on elemental mercury present in the amalgam.[8] As a means of understanding the chemistry involved in the second reduction process (Figure 1), we carried out reductions using sodium-naphthalene. This is a more powerful reductant than is sodium amalgam, and the use of sodium−naphthalene with compounds **1**−**3** converts them to the corresponding hydrides $Cp'_2Nb(H)$(L). The source of the hydride ligand is not clear, but it appears that reagents powerful enough to carry out two successive reductions with **1**−**3** convert them to a reactive (highly basic) anion that leads to hydride. This is presumably the reason the second reduction is not fully reversible.

Niobium−Mercury Compounds As Sources of Nb(II) Radicals. The production of heterometallic species **4**−**6** was postulated to result from attack of niobium-centered radicals on elemental mercury.[8] Of greater utility would be the reverse process,[12] for this

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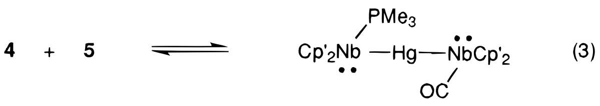
would indicate that these compounds can serve as sources of the radical intermediates. Therefore, we sought evidence for exchange reactions indicating the intermediacy of the radicals. In the first of these, an equimolar mixture of **4** and **5** was dissolved in benzene-d_6 and allowed to equilibrate at room temperature. After ca. 10 h, NMR spectroscopy showed evidence for a new species **7** with inequivalent niobium centers;[8] this was attributed to the exhange reaction depicted in eq 3, a process thought to proceed via the niobium(II) species. To eliminate the (unlikely) possibility that this process involved a double ligand substitution (CO for PMe_3 exchange without Nb−Hg homolysis), we also carried out the exchange reaction depicted in eq 4; note that **4** contains Cp′ ligands while the product (**8**) contains both Cp′ and Cp ligands. A ligand substitution here would involve pairwise exchange of cyclopentadienyl ligands, which is far less likely than homolysis of the metal−metal bond. Thus, the exchange processes shown in eqs 3 and 4 provide convincing evidence indicating that **4**−**6** serve as sources of the $Cp'_2Nb^{II}(L)$ radical. Indeed, we observed a 10-line ESR signal during the production of **4**, indicating the presence of a niobium-centered radical in solution;[8] this signal disappeared as diamagnetic **4** was produced. Also noteworthy is the observation (above) that the radicals do not undergo reduction with sodium amalgam; hence either precursors **1**−**3** or products **4**−**6** may be stirred over excess sodium amalgam for days without exhibiting reduction past the Nb(II) oxidation state.



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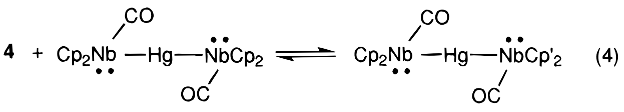
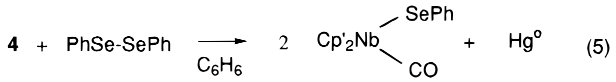


8

Radical Reactions and the Formation of Nb−X Bonds. With evidence for the accessibility of radical intermediates, we sought to characterize their synthetic potential. In the first such reaction, **4** or **5** was dissolved in benzene and treated with 1 atm of H_2. Over a period of 1 day at ambient temperature, the compounds were converted smoothly to the known hydrides $Cp'_2Nb(L)(H)$. This constitutes very mild conditions for the homolytic activation of hydrogen by a metal center which is undergoing only a one-electron oxidation; e.g., there is no evidence for oxidation to a niobium(IV) species here. Similarly, if benzene solutions of these same compounds (**4** or **5**) are heated to 100 °C in an evacuated, sealed NMR tube, they also convert cleanly into the hydrides in a few hours; it should be noted that the use of benzene-d_6 also leads to the niobium hydrides, with little or no incorporation of deuterium (as evidenced by ^2H NMR). The C−D bond in benzene is very strong, so we also carried out these thermolyses in toluene-d_8 (or THF-d_8). These reactions also led only the niobium hydride, and deuterium NMR showed no evidence for Nb−D; we have been unable to identify the source of the hydride in these reactions. Finally, photolysis (medium-pressure mercury lamp, ca. 30 min) in benzene-d_6 also led to the production of hydride with no deuterium incorporation. None of these reactions is of synthetic utility, since the hydrides are readily available via other routes. However, they help establish a useful base line for the studies to be noted below. In the absence of a hydrogen atmosphere, compounds **4** and **5** are stable for 1−2 days in solution at ambient temperature. Eventually, they do convert to the hydrides; hence, in the reactions with added reagents discussed below, a negative result (i.e., failure to react with the added reagent) would be indicated by the production of hydride. Only in rare circumstances do **4** and **5** exhibit gross decomposition to intractable products. It is important to note that we have seen no evidence for niobium−niobium bond formation under any circumstances.

Other species with metal−metal bonds have been treated with alkyl halides in an effort to trap radical intermediates.[5a,13] Indeed, reaction of **4**−**6** with $CDCl_3$ leads first to the precursors **1**−**3** and then to the known compound Cp'_2NbCl_2.[14] Although we have not proved that this is a radical-induced reaction, it nonetheless suggested studies on the behavior of the mercury adducts with other potential radical precursors. Thus, we treated compound **4** with Ph_2Se_2 to look for Nb−Se bond formation; Ph_2Se_2 is an excellent trapping reagent for organic radicals and reacts with primary alkyl radicals with rate constants of ca. 10^7 M^{-1} s^{-1}.[15] Indeed, reaction of **4** with diphenyldiselenide (eq 5) gives rise to the niobium−selenium compound **9** within 15 min at room temperature; this reaction is quite clean and gives no other niobium-containing products, but an excess of the diselenide converts mercury to $Hg(SePh)_2$.[16] Compound **9** exhibits the expected ^1H NMR resonances for Cp′ and phenyl groups, a ^{77}Se NMR signal at −44.6 ppm, and an infrared stretch for the CO ligand at 1926 cm^{-1}. Compound **9** could also be prepared by treatment of **1** with Na^+PhSe^- in THF, but the low solubility of this salt meant that this metathesis reaction required days to go to completion. A related reaction of **4** with dibenzyldiselenide gave a mixture of at least two products, one of which was the known $Cp'_2Nb(CO)(CH_2Ph)$.[17] Diselenides are known to exhibit weak Se−Se bonds with BDEs of ca. 44 kcal/mol, and



9

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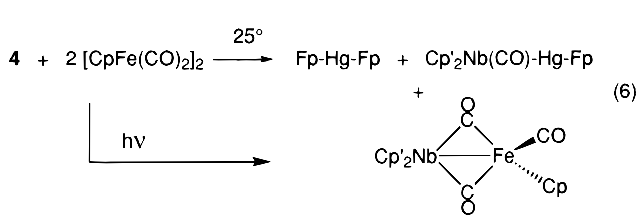
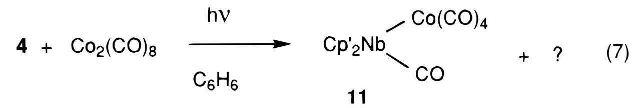
this makes them susceptible to radical reactions;[15] this is undoubtedly the reason for the formation of **9** in eq 5, since homolysis of the Se−Ph bond would not be likely. However, the benzyl radical is considerably more stable than is the phenyl radical,[18] and homolysis of the Se−benzyl bond could, and presumably does, result in the production of the niobium−benzyl species.

Preparation of New Heterometallics. In a recent review, it was noted that there exist relatively few niobium-containing heterobimetallic species.[19] Clearly, radical cross-coupling reactions represent a potentially useful synthetic route to such species, albeit one that is often limited by competition with self-coupling reactions leading to homonuclear metal−metal dimers. Since the niobium species under study are not prone to this latter process, we sought evidence for their use in the formation of heterobimetallic species. In one such attempt, equimolar quantities of $[CpFe(CO)_2]_2$ (Fp_2, a potential source of $Fp^\bullet$) and **4** were reacted in benzene at 25 °C. After a period of of ca. 20 h, ^1H NMR suggested the formation of the three products shown in eq 6; the ratios vary with subtle details of the experiment, but **10** is usually the major product. The mixture contains the known mercury adduct Fp_2Hg,[12] a product tentatively identified as a Nb−Hg−Fe species (this assignment is made difficult by the fact that the mixture is not easily separable), and new compound **10**. While this reaction indicated the reactivity of the Nb−Hg compounds, it was of little synthetic value. However, when the same reaction was run under photochemical conditions using a medium-pressure mercury lamp, several changes were noted; the reaction went to completion much more quickly (45 min of photolysis), elemental mercury was deposited in the bottom of the vessel, and **10** was the sole product. Compound **10** was obtained as violet needles, which were deposited from a saturated hexane solution cooled to −20 °C. It exhibited infrared bands at 1907 and 1698 cm^{-1}, indicating the presence of both bridging and terminal carbonyl ligands. The ^1H NMR spectrum contained a resonance for the iron-bound Cp ligand and two resonances for the aromatic hydrogens of the niobium-bound Cp′ ligands; since each of these Cp′ ligands contains two pairs of diastereotopic protons (one set α to the $SiMe_3$ substituent and one set *β*), two sets of Cp′ signals would seemingly require the presence of two mirror planes in **10**. This is not the case, and the spectral data were rationalized with X-ray crystallography and VT-NMR studies; the results of these will be presented below.



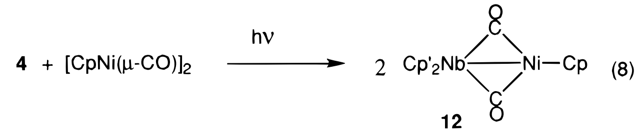
10

As a probe of the generality of the chemistry in eq 6, **4** was allowed to react with other homonuclear dimers. Equimolar quantities of **4** and $Co_2(CO)_8$ reacted readily under similar photochemical conditions, within 25 min giving rise to a new compound exhibiting infrared bands at 2029, 1966, 1949, and 1906 cm^{-1} and NMR signals at 5.07 and 4.59 ppm. There is no evidence for bridging carbonyls, and we assign the 1906 cm^{-1} band to the Nb-CO ligand. The structure proposed for the major product is shown in eq 7. Unfortunately, the production of this compound was always accompanied by the formation of an additional product which exhibited NMR signals 5.12 and 5.60 ppm; this was usually a minor product but was always present. The infrared signature of this minor product was largely masked by the strong bands of the major product; since we were unable to separate these products, we are unable to identify the minor product; it is worth noting that an earlier study of some similar Nb−Co heterometallics show evidence of unusual spectral data and facile isomerization.[20] A related reaction with $[CpNi(\mu\text{-}CO)]_2$ proceeded as indicated in eq 8;[21] here, photolysis for 45 min gave the green **12** as the only metal-containing product. Compound **12** exhibited a single infrared band at 1745 cm^{-1} and ^1H NMR resonances for the Ni−Cp (5.33 ppm) and Nb−Cp′ ligands (4.90, 4.23 ppm); this compound *is* expected to contain two mirror planes, so the spectral data are fully consistent with the formulation given in eq 8. The success of these photochemical routes suggests that products **10**−**12** result because they are stable to photolysis; this was confirmed for **10**, which only exhibited *slow* photochemical conversion to an unknown compound over a period of several hours.



$$\mathbf{4} + Co_2(CO)_8 \xrightarrow[C_6H_6]{h\nu} Cp'_2Nb(Co(CO)_4)(CO) + ? \qquad (7)$$

11



$$\mathbf{4} + [CpNi(\mu\text{-}CO)]_2 \xrightarrow{h\nu} 2\ Cp'_2Nb(\mu\text{-}CO)_2Ni{-}Cp \qquad (8)$$

12

Crystallographic Study of 10. The violet needles of **10** were found to diffract satisfactorily, and the results of an X-ray study are shown in Figure 2. Crystal data and key bond lengths and angles are presented in Tables 1 and 2. Compound **10** crystallized in the trigonal space group $P3_2$ with three molecules per unit cell. As indicated in eq 6, the molecule consists of niobium and iron fragments connected with a Nb−Fe bond and two bridging carbonyl ligands. The Nb−Fe separation is 2.8156(6) Å; this is less than the sum of the covalent radii (3.00 Å), and the presence of the metal−metal bond presumably accounts for the diamagnetism seen for **10**. The four-membered ring is approximately planar, with torsion angles of 2.40(14)° (C(1)−Nb(1)−C(2)−Fe(1)), 176.6(2)° (C(2)−Nb(1)−Fe(1)−C(1)), and 2.7(2)° (Nb(1)−C(2)−Fe(1)−C(1)). The bridg-

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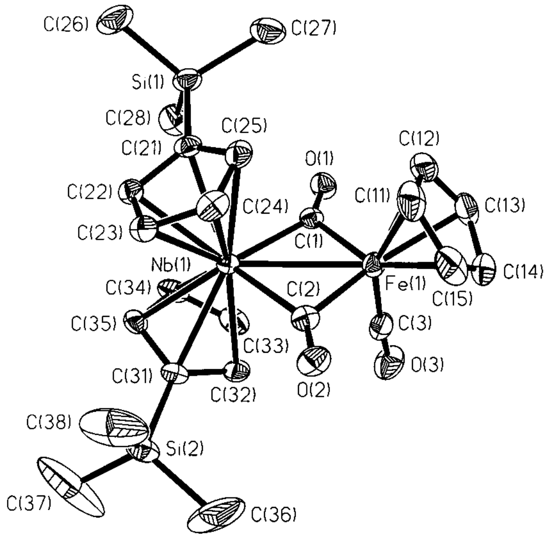

Figure 2. ORTEP drawing of the structure of **10** showing the atom-numbering scheme.

ing carbonyls exhibit Nb−C distances of 2.183(4) and 2.184(4) Å, Fe−C distances of 1.969(4) and 1.997(4) Å, Nb−C−Fe angles of 85.23(14)° and 84.5(2)°, Nb−C−O angles of 144.1(3) and 144.4(3)°, Fe-Nb−C angles of 44.17(9)° and 44.92(11)°, Nb−Fe−C angles of 50.59(11)° and 50.53(1), and Fe−C−O angles of 130.6(3)° and 131.0(3)°. Thus, with the exception of the Fe−C distances and Fe−Nb−C angles, the two carbonyl ligands exhibit identical (to within 3σ) metrical parameters; it is also clear that the carbonyl ligands lean toward the iron center and away from the niobium center. Crabtree has reviewed structural data for bridging carbonyls[22] and has suggested that bridging and semibridging carbonyls may be identified by comparison of the angles θ (M−C−O) and ψ (M−M−X). Within this framework, symmetrically-bridging ligands show θ and ψ parameters near 138° and 49° (with ranges of ca. 136−144° and 44−52°) and bent semibridging ligands show θ and ψ ranges of 136−180° and 50−75°. As such, it is clear that **10** ($\theta = 144.2(2)°$, $\psi = 44.5(4)°$) does not exhibit metrical parameters within the ranges normally associated with semibridging carbonyls, even though there is a slight distortion in that direction; the two carbonyls in **10** are best described as bridging, not semibridging.

Variable-Temperature NMR Studies of 10. The NMR spectral data for **10** were not consistent with the solid-state structure, and comparison with the cobalt or nickel compounds indicates that bridged and nonbridged structures are accessible. We undertook a variable-temperature NMR study of **10** with the aim of understanding the 25° NMR data and to uncover any fluxional processes. At 25 °C, the niobium−Cp′ ligands exhibited two slightly broadened resonances at ca. 4.82 and 4.21 ppm, and these became sharper at 35 °C. However, at temperatures below ca. 0 °C these decoalesced into four signals; this is consistent with the solid-state structure of **10**, since the static structure has one mirror plane (not two) and would have inequivalent Cp′ ligands. Fortunately, the two pairs of signals exhibited unequal chemical shift differences and decoalesced at different temperatures; the signal at 4.21 decoalesced at ca. 9 °C, while the signal at 4.82 decoalesced at ca. 2 °C. This gave rate constants at two temperatures, and 2D-EXSY (exchange spectroscopy)[23] was utilized to determine rate constants at temperatures down to −50 °C; these rate constants are listed in Table 3, and the corresponding Eyring plot is given as Figure 3. It is clear that rate constants obtained in these two ways (EXSY and coalescence) fit the same line, and the resulting activation parameters for the fluxional process are $\Delta H^{\ddagger} = 15.1(7)$ kcal/mol and $\Delta S^{\ddagger} = 6.8(8)$ cal mol^{-1} deg^{-1}. This serves to reconcile the solution and solid-state data, and it is clear that the infrared spectrum consists of a Fe−CO (terminal) stretch and the antisymmetric stretch for the bridging carbonyls.

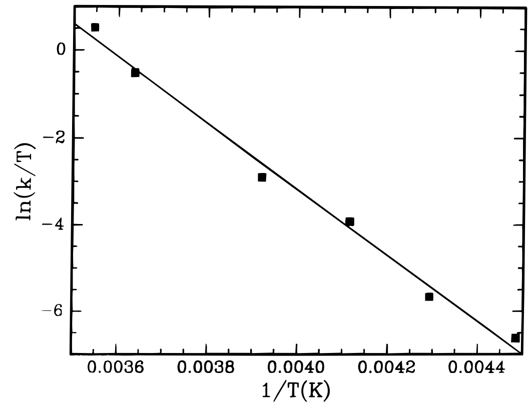

Figure 3. Erying plot for the fluxionality in **10** in toluene-d_8.

Table 3. Kinetic Data for Fluxionality in 10 (See Text)

temp (°C)	k (s^{-1})
9	474
2	164
−18	14.0
−30	4.80
−40	0.80
−50	0.29

Reactions with Two-Electron Ligands. In the processes described above, the niobium(II) radicals reacted with other radical sources to produce species most reasonably formulated as Nb(III) compounds. However, niobocene derivatives containing Nb(IV) are also well-known,[24] so we attempted a few reactions with potential two-electron ligands. In the first of these, a benzene solution of **4** was treated with excess paraformaldehyde and the solution was irradiated for 30 min. At the end of this time, the ^{1}H NMR indicated the absence of diamagnetic species and infrared showed no evidence for the presence of the niobium-bound carbonyl ligand. Indeed, an ESR study of this solution indicated that the reaction had proceeded with formation of the known niobium−formaldehyde adduct $Cp'_2Nb(\eta^2\text{-}CH_2O)$; we have previously prepared this compound by reduction of the complex $Cp'_2Nb(Cl)(\eta^2\text{-}CH_2O)$, which loses chloride upon reduction.[25] Thus, the reaction proceeded as shown in eq 9, and complexation of the formaldehyde ligand resulted in loss of the carbonyl ligand. In a

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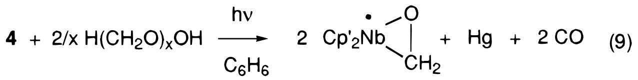
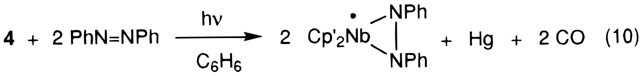


$$\mathbf{4} + 2/x\ H(CH_2O)_xOH \xrightarrow[C_6H_6]{h\nu} 2\ Cp'_2\dot{N}b(\eta^2\text{-}OCH_2) + Hg + 2\ CO \quad (9)$$

similar vein, compound **4** was also treated with azobenzene and irradiated for 45 min. This reaction gave a green paramagnetic product **13** which exhibited the 10-line ESR spectrum typical for niobium complexes (^{93}Nb, 100%, $I = {}^9/_2$), with a g value of 1.9888 and $\langle a \rangle_{Nb} = 10$ G. The infrared spectrum again indicated that the carbonyl ligand had been lost, and this reaction is proposed to yield the azobenzene complex **13** shown in eq 10. We were unable to crystallize this compound



$$\mathbf{4} + 2\ PhN{=}NPh \xrightarrow[C_6H_6]{h\nu} 2\ Cp'_2\dot{N}b(\eta^2\text{-}PhNNPh) + Hg + 2\ CO \quad (10)$$

13

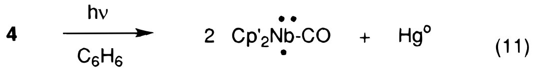
(which oils out of all common solvents), and the Nb(V) precursor $Cp'_2Nb(Cl)(\eta^2\text{-}PhNNPh)$ is unknown. However, reaction of the dimeric Nb(III) reagent $[Cp'_2Nb(\mu\text{-}Cl)]_2$ with azobenzene yielded a precipitate of Cp'_2NbCl_2; we filtered off the insoluble Cp'_2NbCl_2 and determined that **13** remained in solution. Hence, while the azobenzene is unable to give symmetrical cleavage of the niobium(III) dimer $[Cp'_2Nb(\mu\text{-}Cl)]_2$, it effects asymmetric cleavage to yield **13**. This latter reaction constitutes the preferred route to **13**, but the reactions shown in eqs 9 and 10 indicate that the Nb(II) radical species are capable of releasing a carbonyl ligand to accommodate an incoming π-bound ligand and formal two-electron oxidation.

Discussion

Thermal and Photochemical Routes to Radicals. The exchange reactions depicted in eqs 3 and 4 indicate that the Nb−Hg compounds serve as sources of Nb(II) radicals. The reactions with dimeric species such as Fp_2 (eq 6) suggest that thermal and photochemical routes can exhibit differing synthetic outcomes, but we believe they are similar in proceeding via Nb(II) radicals. They contrast, however, in two important ways. First, the photochemical reaction with Fp_2 requires less time to go to completion than does the thermal one. Second, the photochemistry yields only **10**, while the thermal reaction gives three products. This suggests that the photochemistry serves to generate a higher concentration of Nb(II) radicals while also resulting in the loss of elemental mercury. Indeed, others have noted the utility of photochemical approaches in the elimination of mercury from heterobimetallic species. In a study of $Hg[Co(CO)_4]_2$, it was noted that this compound exhibited an absorption band at 328 nm (ϵ ca. 25 000 L mol^{-1} cm^{-1}), and this was assigned to a transition involving the linear Co−Hg−Co framework.[26] The Hg−Co bonds in this species are polarized and exhibit $Hg^+{-}Co^-$ character; thus, either a $\sigma{-}\sigma^*$ or $d_{Co}{-}\sigma^*$ transition would have a significant component of Co → Hg charge transfer (MMCT) character. Similarly, the cluster anion $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ consists of two Os_9C carbide clusters separated by a triangular Hg_3 moiety; this exhibited an absorption band at 540 nm (ϵ 43 800 L mol^{-1} cm^{-1}) which was also thought to be localized in the metal−metal bonding framework.[27] Irradiation into these absorption bands gives extrusion of elemental mercury in both cases, leading to production of $Co_2(CO)_8$ in the first case and $[Os_{18}Hg_2C_2(CO)_{42}]^{2-}$ in the second. By comparison, the UV−vis spectrum of Nb−Hg compound **5** exhibits a shoulder at 514 nm (ϵ 4390 L mol^{-1} cm^{-1}). This band is partially obscured by a strong LMCT band centered at 350 nm, and we do not observe the MMCT band for **4**; we believe it is blue-shifted (relative to **5**) and is obscured by the LMCT band. The MMCT band of **5** tails into the visible region of the spectrum and is responsible for the orange color of the compound; the strength of the transition is indicative of charge-transfer character. It is interesting to note that the energy of the transition for **5** is between those of $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ and $Hg[Co(CO)_4]_2$. Thus, the transition energy for **5** is more comparable to that of the anionic osmium cluster, and it is clear that the niobium moieties are considerably more electron-rich than are the $Co(CO)_4$ moieties.

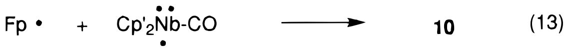
Mechanistic Considerations. A detailed, quantitative understanding of the mechanism for the photoprocesses described herein is not yet available because the Nb−Hg compounds exhibit broad UV−vis bands that strongly overlap those exhibited by the other dimeric species used. Hence, we are unable to eliminate the possibility of simultaneous photoprocesses generating multiple reactive intermediates. We are seeking other substrates which are suitable for detailed photophysical and mechanistic studies, and these will be reported later. However, for the present, we may compare the photochemical and thermal results to offer general mechanistic hypotheses. In so doing, we will focus on the Nb−Fe system for which the supporting information (e.g., on the chemistry and photochemistry of Fp_2) is most readily available.

The reaction of **4** and Fp_2 involves *two* photosensitive reagents, and irradiation could generate both Cp'_2NbL and Fp radicals.[28] Hence, eqs 11−13 constitute a simple mechanism for the production of **10**, involving simultaneous generation of these radical species. It is



$$\mathbf{4} \xrightarrow[C_6H_6]{h\nu} 2\ Cp'_2\ddot{\underset{\bullet}{N}}b\text{-}CO + Hg^{\circ} \quad (11)$$

$$Fp_2 \xrightarrow[C_6H_6]{h\nu} 2\ Fp^{\bullet} \quad (12)$$



$$Fp^{\bullet} + Cp'_2\ddot{\underset{\bullet}{N}}b\text{-}CO \longrightarrow \mathbf{10} \quad (13)$$

entirely possible that this sequence contributes to the production of **10**, but it cannot be the only mechanism operating. First, we noted above that photolysis of **4** alone yields the hydride $Cp'_2Nb(H)(CO)$; thus, the low steady-state concentration of Fp radical (which recom-

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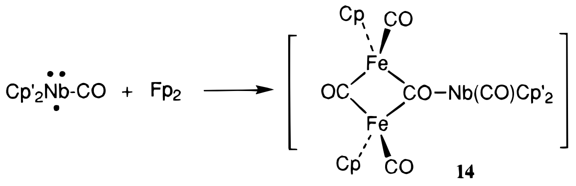
bines with $k = 4.5(2) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$)[27c] should lead to inefficient coupling of the Nb and Fp radicals and the production of substantial amounts of the niobium hydride; it does not. In addition, the *thermal* route to **10** must proceed without the prior generation of Fp radical, since this homolysis reaction has been shown to have a half-life of ca. 30 days.[29] Hence, we propose that the Nb(II) radical serves as the reactive intermediate and that it reacts with intact $\mathrm{Fp_2}$ as well as (perhaps) Fp radical.

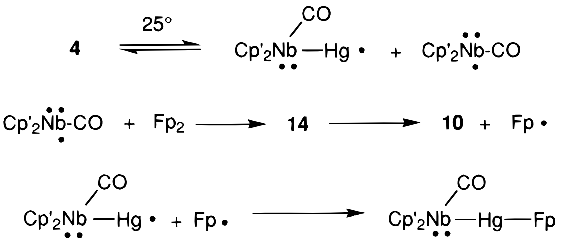
There are detailed studies on the reactions of radicals with metal−metal dimers, and these have exhibited two common characteristics; the reactions are electron-transfer in nature, and the reductant is a 19-electron species formed via ligand addition to the 17-electron radical (eq 1). A similar process is likely in the production of **10**, but no ligand has been added to convert $\mathrm{Cp'_2Nb{-}CO}$ into a 19-electron reductant. The reactions are typically carried out in benzene, which is a poor ligand for the bent metallocene; related $\mathrm{Cp'_2NbL}$ fragments bind alkynes readily,[30] but styrene[31] and formaldehyde[25] adducts are the only known examples of complexes of ligands containing $\mathrm{sp^2}$-hybridized carbon donor atoms. Hence, the only potential ligand for the niobium center is $\mathrm{Fp_2}$ itself, which is known to bind Lewis acids at the oxygen of the μ-carbonyl ligand; indeed, other heterometallic complexes of metal carbonyl clusters have been characterized crystallographically and show binding of the electrophilic metal center(s) in this way.[32] Rather than invoke an electron-transfer reaction that generates a 16-electron niobium center, we therefore propose the formation of the $\mathrm{Fp_2}$−niobium adduct **14** as a precursor to reduction of the $\mathrm{Fp_2}$ (eqs 14 and 15). In this way, an intramolecular charge-transfer process generates **10** and releases 1 equiv of Fp radical. This can then couple to make a second equivalent of **10** or $\mathrm{Fp_2}$. This postulate is preferable to direct attack of the niobium radical on an iron center, as we are unaware of any precedent for a radical attack (at iron) leading to homolysis of the $\mathrm{Fp_2}$ dimer.



(14)

$$[\mathbf{14}] \longrightarrow \mathbf{10} + \mathrm{Fp}^{\bullet} \quad (15)$$

A very similar mechanism can be invoked to explain the thermal reaction, which differs in the sense that the mercury is retained in some of the products. Indeed, the exchange processes depicted in eqs 3 and 4 never show visible evidence for loss of elemental mercury; for this reason, we depict the thermal Nb−Hg homolysis as a stepwise process which leaves one such linkage intact (eq 16). The $\mathrm{Cp'_2Nb{-}CO}$ radical is proposed to react with $\mathrm{Fp_2}$ as before to form **10** and $\mathrm{Fp}^\bullet$ via adduct **14** (eq 17). Subsequently, the $\mathrm{Fp}^\bullet$ radical couples with the mercury-centered radical to generate the Nb−Hg−Fp product (eq 18). Although omitted to save space, subsequent Nb−Hg homolyses involving this species would lead to Fp−Hg−Fp. Thus, the thermal reaction to **10** is proposed to involve the same mechanism as does the photochemical process; the overall reaction differs only in that it retains mercury in the $\mathrm{Nb{-}Hg}^\bullet$ radical, and this is the source of the mercury-containing final products.



$$\mathbf{4} \underset{}{\overset{25°}{\rightleftharpoons}} \mathrm{Cp'_2Nb(CO){-}Hg^{\bullet}} + \mathrm{Cp'_2Nb{-}CO^{\bullet}} \quad (16)$$

$$\mathrm{Cp'_2Nb{-}CO^{\bullet}} + \mathrm{Fp_2} \longrightarrow \mathbf{14} \longrightarrow \mathbf{10} + \mathrm{Fp}^{\bullet} \quad (17)$$

$$\mathrm{Cp'_2Nb(CO){-}Hg^{\bullet}} + \mathrm{Fp}^{\bullet} \longrightarrow \mathrm{Cp'_2Nb(CO){-}Hg{-}Fp} \quad (18)$$

The proposed mechanisms are consistent with all of the synthetic and control reactions carried out to date, they relate the thermal and photochemical results in a simple way, and they are consistent with the large body of evidence favoring 19-electron reductants in related reactions.[3,4] While we believe they constitute the major routes to the observed products, we note again the possiblity of secondary photochemical routes that constitute alternate pathways to the observed products; identification of these will require detailed kinetic and photophysical studies and will be the subject of future work.

Structural Properties. We noted earlier that in comparison to other transition metals, there are relatively few niobium-containing heterometallics.[18] Nonetheless, these have exhibited a wide-ranging structural diversity, and **A**,[33] **B**,[34] **C**,[20,35] and **D**[36] indicate the structure types known for niobium−metal compounds. Although only four bonding modes are indicated, there

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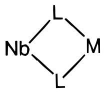
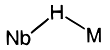
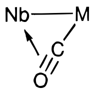


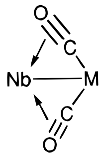
A



B



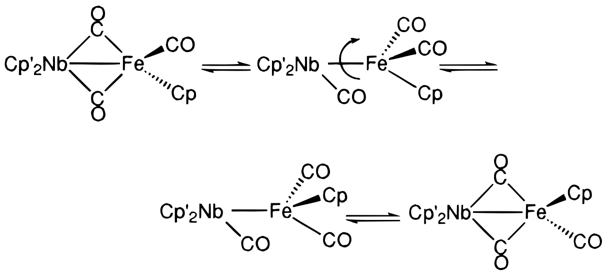
C



D

is considerable variation within these groups (beyond simply the identity of the ancillary ligands on the two metal centers). For example, compounds of type **A** contain two bridging ligands L, but these may be neutral (CO),[33e] monoanions (SR, SeR, or PR_2),[33a−e,g] or dianions (S),[33f] and there may or may not be a niobium−metal bond. Compounds **C** and **D** are characterized by the presence of semibridging carbonyl ligands, and these may be linear or bent. The existence of types **A**, **C**, and **D** suggests that there may be relatively small barriers to isomerizations involving carbonyl ligands. Although this hypothesis has not been tested previously, compound **10** proved to be amenable to such a study. The resulting $\Delta G^{\ddagger}$ (13.1 kcal/mol) compares closely with that observed for *cis*−*trans* isomerization in $[CpFe(CO)_2]_2$ ($\Delta G^{\ddagger}$ 10.4 kcal/mol),[37] a process believed to proceed by way of bridge−terminal interconversion and twisting about the metal−metal bond. In addition, our small value for $\Delta S^{\ddagger}$ (6.8(8) cal mol^{-1} deg^{-1}) is not consistent with a heterolysis process yielding the ions $[Cp'_2Nb(CO)]^+$ and $[CpFe(CO)_2]^-$. Nonetheless, we tested for this process by dissolving **10** in acetonitrile and recording the IR spectrum; this polar solvent is known to facilitate the formation of free ions,[38] but we saw no evidence for loss of the bridging carbonyl ligands in **10**. Therefore, we propose that **10** behaves as does $[CpFe(CO)_2]_2$ and equilibrates by way of the process depicted in eq 19.

Conclusions. The niobium−mercury compound **4** shows clear evidence for the generation of electron-rich niobium(II) radicals, and this has proved useful in the preparation of a variety of new organoniobium complexes. The radical species are available via thermal and photochemical paths, and the subsequent chemistry differs mainly in the fate of the mercury. Photochemistry constitutes a facile route for the elimination of the mercury, thus rendering the Nb−Hg compounds a useful means of storing the radicals. Further, the inaccessibility of Nb−Nb bond formation makes the radicals highly reactive toward a variety of substrates. Their reaction with metal−metal dimers is related to the radical-induced disproportionation of these dimers,[3] with one notable exception. In cases in which a dimer $L_nM{-}ML_n$ is reduced by the action of radical $L_nM^{\bullet}$, the latter first adds a ligand L′; the net result is production of $L_nL'M^+$ and L_nM^-, an ion pair containing two 18-electron species. In the chemistry reported herein, the 17-electron niobium-containing radical leads to heterometallic species **10**−**12** in the absence of added ligand and we have postulated the intermediacy of an adduct (**14**) to facilitate the process. Inasmuch as the heterometallic species **10**−**12** appear to have low barriers to interconversion of bridging and terminal carbonyls, we expect them to have a rich chemistry. Future work will be devoted to a study of potential associative processes involving the niobium(II) radicals and added ligands, of reactions of the radicals with other metal centers which do not contain carbonyls to support bridging interactions, and on the chemistry of adducts such as **10**−**12** toward small molecules.



(19)

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Supporting Information Available: Text giving a summary of the crystallographic analysis, tables of crystal data, bond lengths and angles, atomic coordinates, and thermal parameters, and an ORTEP diagram of **10** (16 pages). Ordering information is given on any current masthead page.

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