Reactivity of a Phosphido-Niobocene Derivative toward CS_2 and Alkyl Halides to Give Phosphinodithioformato- and Phosphino-Niobocene Complexes: X-ray Crystal Structures of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-S-SC(S)(PPh}_2))(CO)]$ and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CO)]I_3$

Antonio Antiñolo,* Santiago García-Yuste, Antonio Otero,* Juan C. Pérez-Flores, Rebeca Reguillo-Carmona, Ana M. Rodríguez, and Elena Villaseñor

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Quimica, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain

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The reaction of the niobocene complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(CO)]Cl$ (**1**) with NaOH yielded the corresponding phosphidoniobocene derivative $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]$ (**2**) by deprotonation of the P−H bond. The subsequent insertion reaction of carbon disulfide into the Nb−P bond yielded the first examples of a diphenylphosphinodithioformato ligand coordinated to the niobocene system by giving $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-S-SC(S)(PPh}_2))(CO)]$ (**3**) and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^2\text{-S,S-SC(S)(PPh}_2))]$ (**4**); the latter compound can also be prepared by the corresponding CO elimination of **3**. The cationic d^2 species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(CO)]X$ (R = Me, X = I (**5**); CH_2Ph, X = Br (**6**); CH_2CH_2Ph, X = Br (**7**)) were prepared by the reaction of alkyl halides RX (R = Me, X = I; CH_2Ph, X = Br; CH_2CH_2Ph, X = Br) with **2** by electrophilic attack on the phosphorus atom present in the phosphido terminal ligand. In the same way, the reaction of **2** with ICH_2CH_2I yielded the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CO)]I_3$ (**8**). The molecular structures of **3** and **8** were determined by single-crystal X-ray diffraction studies.

Introduction

Dithiocarbamato ligands, $R_2NCS_2^-$, have attracted considerable attention in coordination chemistry,[1] mainly due to their ability to form stable chelate complexes. However, very little effort has been directed toward investigating the analogous dialkylphosphinodithioformato ligands, $R_2PCS_2^-$. Indeed, only a few well-characterized $R_2PCS_2^-$-containing complexes of early-middle transition metals such as Zr,[2] Mo,[3] and W[4,5] have been reported to date, and in these complexes, the ligand coordinates to metal centers through the two S atoms[2] (**a**), the P and S atoms by chelation[5a] (**b**), and either simple S- or P-coordination[5b] (**c** and **d**) (see Figure 1).

A few years ago, we reported the synthesis of a new family of complexes including $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)L]Cl$ (**1**), where L = CO, CNR,[6] and these were prepared by an insertion reaction of $ClPPh_2$ into the Nb−H bond of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)L)]$. Treatment of derivative **1** with aqueous NaOH yielded the corresponding neutral phosphidoniobocene complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]$ (**2**) by deprotonation of the P−H bond.[7] This complex represents an interesting starting material to extend the phosphorus-containing niobocene chemistry. The phosphorus atom from the phosphido terminal ligand has a lone electron pair that is expected to give rise to interesting chemistry that can be explored. We focused our attention on the synthesis of new phosphorus-containing niobocene complexes from **2** by exploring the possibilities for both the insertion reaction into the Nb−P bond, using carbon disulfide as the reagent, and the electrophilic attack on the P atom of the phosphido terminal ligand in alkylation processes with several RX reagents. The first type of reactivity has allowed the preparation of the new niobocene containing the anionic diphenylphosphinodithioformato ligand, $Ph_2PCS_2^-$, namely, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-S-SC(S)(PPh}_2))(CO)]$ (**3**) and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^2\text{-S-SC(S)(PPh}_2))]$ (**4**), and the second one, the isolation of a new family of cationic d^2 18-electron complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(CO)]X$ (R = Me, X = I (**5**); CH_2Ph, X = Br (**6**); CH_2CH_2Ph, X = Br (**7**)). Finally, the reaction of **2** in the presence of ICH_2CH_2I gave $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CO)]I_3$ (**8**).

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* To whom correspondence should be addressed. E-mail: antonio.antinolo@uclm.es; antonio.otero@uclm.es. Fax: +34926295318.

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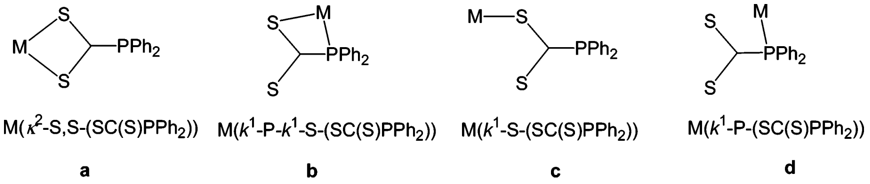
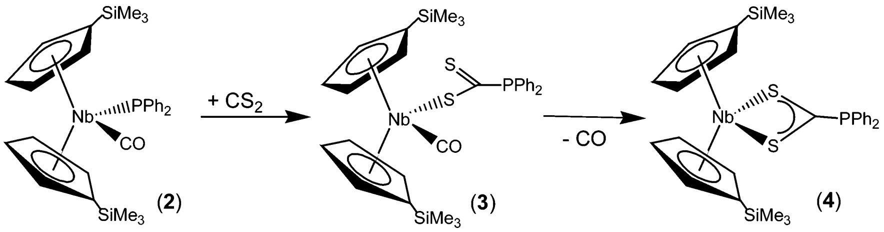


Figure 1. Coordination modes of the $Ph_2P(S)CS^-$ ligand.

Scheme 1



Results and Discussion

Synthesis and Characterization of Diphenylphosphinodithioformato-Containing Complexes. We previously reported the synthesis of the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(CO)]Cl$ (**1**), which was prepared by an insertion reaction of $ClPPh_2$ into the Nb−H bond of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(CO)]$.[6] In the study described here it was envisaged that $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]$ (**2**) would be obtained by deprotonation[7] of the P−H bond of **1**. In fact, the preparation of the phosphidoniobiocene complex **2** was achieved by deprotonation of the $PHPh_2$ ligand present in the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(CO)]Cl$ (**1**) with aqueous NaOH (eq 1).

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)(CO)]Cl\ (\mathbf{1}) \xrightarrow[\substack{-\,NaCl \\ -H_2O}]{+\,Na(OH)} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]\ (\mathbf{2}) \qquad (1)$$

Complex **2** was isolated as a yellow-brown oil that was air-sensitive and insoluble in most organic solvents. Complex **2** was characterized by IR and ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectroscopy. The IR spectrum of **2** shows one band at 1918 cm^{-1}, and this corresponds to $\nu(C{\equiv}O)$ of the carbonyl ligand. A band corresponding to $\nu(P-H)$ of the P−H bond was not observed in the IR spectrum, which is consistent with the conversion of the coordinated diphenylphosphine ligand to a new phosphido ligand. Further evidence for this transformation was provided by the ^1H NMR spectrum, which did not contain the doublet corresponding to the P−H bond at ca. 7 ppm that is present in the parent complex **1**.[6] Evidence for the presence of a new phosphido ligand was provided by the ^{31}P NMR spectrum, which contains a singlet at δ −10.8 ppm due to the PPh_2 ligand.[7] This latter signal is at higher field than that in the corresponding $PHPh_2$ ligand in complex **1**, which shows the greater electron density on the P atom in the neutral phosphido ligand. At low field the $^{13}C\{^1H\}$ NMR spectrum exhibits one signal at δ 260.0 ppm for the carbonyl ligand. The spectroscopic data are in agreement with an 18-electron d^2 niobocene species in which the phosphido terminal ligand is coordinated as a monoanionic donor ligand. Thus, the phosphorus atom of the phosphido ligand retains one electron pair, and this makes it susceptible to further electrophilic attack. The niobium atom must adopt a pseudo-tetrahedral structure with both cyclopentadienyl rings bonded in a η^5-coordination mode to give the typical bent metallocene conformation.

The new diphenylphosphinodithioformato-containing niobocene $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-}S\text{-}SC(S)(PPh_2))(CO)]$ (**3**) was prepared by stirring a mixture of **2** with carbon disulfide for 4 h. This reaction, after the appropriate workup procedure, gave complex **3** as a red solid. However, when the reaction was carried out in thf over a longer period of time, the solution became dark green and the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^2\text{-}S,S\text{-}SC(S)(PPh_2))]$ (**4**) was isolated after the appropriate workup (see Scheme 1).

In accordance with the different coordination modes for the phosphinodithioformato ligand depicted in Figure 1, situations **c** and **a** are proposed for complexes **3** and **4**, respectively (Scheme 1).

The new derivatives **3** and **4** were isolated as air-sensitive solids and were characterized by IR and NMR spectroscopy. Furthermore, the molecular structure of complex **3** was determined by X-ray diffraction. The IR spectra of **3** and **4** each display a characteristic band at ca. 1000 cm^{-1}, which is due to $\nu(C{=}S)$. However, only the IR spectrum of **3** contains the band due to the $\nu(CO)$, and this is seen at 1927 cm^{-1}. The ^1H NMR spectra contain four multiplets for **3** and two multiplets for **4**, and these correspond to the cyclopentadienyl ligands; these signals are consistent with an asymmetrical and symmetrical environment for the niobium center[8] in these complexes, respectively (see Scheme 1). Further evidence for this situation is provided by the $^{13}C\{^1H\}$ NMR spectra of the complexes, which contain five and three resonances corresponding to the cyclopentadienyl ligands. In addition, a very low field resonance is present in each $^{13}C\{^1H\}$ NMR spectrum, and this appears as a doublet centered at δ 264.0 ($^1J_{CP} = 47.62$ Hz) and 244.0 ppm ($^1J_{CP} = 20.00$ Hz), respectively, for **3** and **4**. These signals correspond to the carbon atom of the diphenylphosphinodithioformato ligand. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of **3** shows a signal at δ 254.6 ppm that is typical of a CO ligand. Finally, the ^{31}P NMR spectra each contain a broad signal, at δ 46.9 ppm as a multiplet for **3** and at δ 2.03 ppm as a quintuplet ($^3J_{PH} = 7.30$ Hz due to phosphorus coupling with the *ortho* hydrogen atoms of the phenyl group) for **4**. The crystal structure of **3** was determined on crystals obtained by crystallization from hexane and confirms the structural arrangement described above.

X-ray Diffraction Study of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-}S\text{-}SC(S)(PPh_2))(CO)]$ (3). The ORTEP diagram obtained by X-ray diffraction of **3** is shown in Figure 2. To the best of our knowledge, the molecular structure of complex **3** represents the first example of an early transition metal where a diphenylphos-

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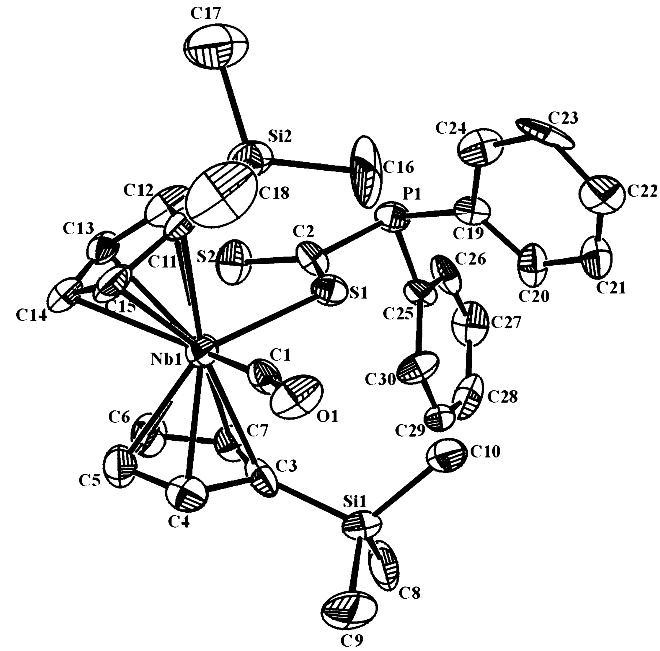

Figure 2. Molecular structure of **3** with 30% probability ellipsoids. Hydrogen atoms have been omitted.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 3 and 8

[Nb(η^5-$C_5H_4SiMe_3$)$_2$ (κ^1-S-SC(S)(PPh$_2$))(CO)] (**3**)		[Nb(η^5-$C_5H_4SiMe_3$)$_2$ (P(I)Ph$_2$)(CO)]I$_3$ **(8)**	
Nb(1)−C(1)	1.97(1)	Nb(1)−C(1)	2.069(6)
Nb(1)−S(1)	2.542(5)	Nb(1)−P(1)	2.565(2)
P(1)−C(2)	1.81(1)	I(1)−P(1)	2.472(1)
P(1)−C(19)	1.81(1)	I(2)−I(3)	2.921(2)
P(1)−C(25)	1.84(2)	I(3)−I(4)	2.924(1)
S(1)−C(2)	1.69(1)	P(1)−C(31)	1.823(6)
S(2)−C(2)	1.67(1)	P(1)−C(41)	1.817(6)
O(1)−C(1)	1.19(1)	O(1)−C(1)	1.131(7)
C(1)−Nb(1)−S(1)	88.6(5)	C(1)−Nb(1)−P(1)	87.3(2)
C(4)−Nb(1)−S(1)	121.1(4)	I(2)−I(3)−I(4)	177.39(3)
C(19)−P(1)−C(2)	104.9(7)	C(41)−P(1)−I(1)	101.6(2)
C(19)−P(1)−C(25)	101.9(6)	C(31)−P(1)−I(1)	99.9(2)
C(2)−P(1)−C(25)	102.3(7)	C(41)−P(1)−Nb(1)	118.6(2)
C(2)−S(1)−Nb(1)	112.6(5)	C(31)−P(1)−Nb(1)	115.5(2)
O(1)−C(1)−Nb(1)	173(1)	I(1)−P(1)−Nb(1)	114.55(6)
S(2)−C(2)−S(1)	128.2(9)	O(1)−C(1)−Nb(1)	178.2(5)
S(2)−C(2)−P(1)	114.1(8)		
S(1)−C(2)−P(1)	117.7(8)		

phinodithioformato ligand has a κ^1-S coordination mode. Selected bond distances and bond angles are listed in Table 1.

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with 4 molecules in the asymmetric unit cell. The local coordination geometry around the Nb atom can be described as pseudo-tetrahedral with two cyclopentadienyl rings bonded to the metal in a η^5 mode and sulfur and carbon atoms of the dithioformato and carbonyl ligands, respectively, comprising the immediate coordination sphere. The distances between the metal atom and the centroids of the Cp rings are 2.042(5) and 2.039(5) Å, and the value of the angle Cent(1)−Nb(1)−Cent(2) is 140° (Cent(1) is the centroid of C(3)−C(7) and Cent(2) is the centroid of C(11)−C(15)). These values are typical of bent niobocene derivatives. The Nb(1)−S(1) bond distance is 2.542(5) Å, and this is very similar to those found in other niobocene systems.[9]

Molecular structures of complexes containing the [M-(SC(S)PPh$_3$)]$^+$ moiety are well documented,[10] although molecular structures of related phosphinodithioformato-containing [M-(SC(S)PPh$_2$)] complexes are very rare in the literature.[2,5]

It is worth noting the relative disposition of the Cp′ ligands (Cp′ = $C_5H_4SiMe_3$) with respect to one another. These ligands are eclipsed with the two SiMe$_3$ groups in *cis* positions and coordinated to the Nb atom in the conventional η^5-fashion. The metal atom, the S, and the carbonyl ligand are practically coplanar and bisect the dihedral angle formed by the two Cp′ ligands. The angle between the CO ligand and the sulfur atom, C(1)−Nb(1)−S(1), is 88.6(5)°.

The angle O(1)−C(1)−Nb(1) (173(1)°) is practically linear. The C(1)−O(1) distance is shorter than that of a free CO, and this indicates substantial back-donation from the metal to the coordinated CO ligand. The PCS$_2$ unit is planar. The P atom is pyramidal (the sum of bond angles at the phosphorus atom is 307°). The noncoordinated S(2) atom is in an *exo* disposition with respect to the aforementioned angle C(1)−Nb(1)−S(1). The angles S(2)−C(2)−P(1) (114.1(8)°) and S(1)−C(2)−P(1) (117.7(8)°) show that the phosphorus atom is closer to the S *exo* atom. This is probably due to steric hindrance between the SiMe$_3$ groups situated in this area and the lone pair on the phosphorus atom.

Mechanistic Proposal for Ph$_2$P(S)CS$^-$ Ligand Formation. The mechanistic proposal for Ph$_2$P(S)CS$^-$ ligand formation in complex **3** is represented in Scheme 2.

The formation of the Ph$_2$P(S)CS$^-$ ligand in an insertion reaction can be understood by the interaction between the Nb-PPh$_2$ moiety and the heterocumulene species CS$_2$ (see Scheme 2). Two intermediate species are possible, and both of these evolve to complex **3**. The first possibility (a) involves initial nucleophilic attack of the coordinated phosphido ligand, through the lone electron pair on the phosphorus atom, onto the electron-deficient carbon atom (electrophilic center) of the CS$_2$ to give a zwitterionic intermediate.[5a] This intermediate evolves to **3** by attack of the noncoordinated sulfur atom on the niobium metal center with the simultaneous cleavage of the Nb−P bond. The second possibility (b) is consistent with a four-centered concerted transition state[8] obtained by an intermolecular insertion process involving the Nb−P bond and one of the C═S bonds.

The formation of complex **4** can be envisaged as being the result of attack of the noncoordinated S atom of the k^1-S-diphenylphosphinodithioformato ligand on the Nb atom and concurrent CO ligand elimination. The substitution of the CO ligand in this class of niobocene, i.e., [Nb(η^5-$C_5H_4SiMe_3$)$_2$(κ^1-S-SC(S)H)(CO)],[8] is not a common reaction, but with a ligand other than carbonyl (e.g., P(OR)$_3$[8] or PHPh$_2$[7]) the reaction can take place easily. In this particular case the high stability of derivative **4** probably provides the driving force for the formation of [Nb(κ^2-S,S-SC(S)PPh$_2$)].

Synthesis and Characterization of Cationic d^2 Phosphino-Containing Complexes. In the second part of this article we describe the reactivity of complex **2** toward alkylation processes with several RX reagents as electrophilic species. The reaction of **2** with excess alkyl halide species such as methyl iodide (MeI), benzyl bromide (BzBr), and 1-bromo-2-ethylbenzene (PhCH$_2$CH$_2$Br) gives d^2 18 e$^-$ cationic phosphinoniobocene

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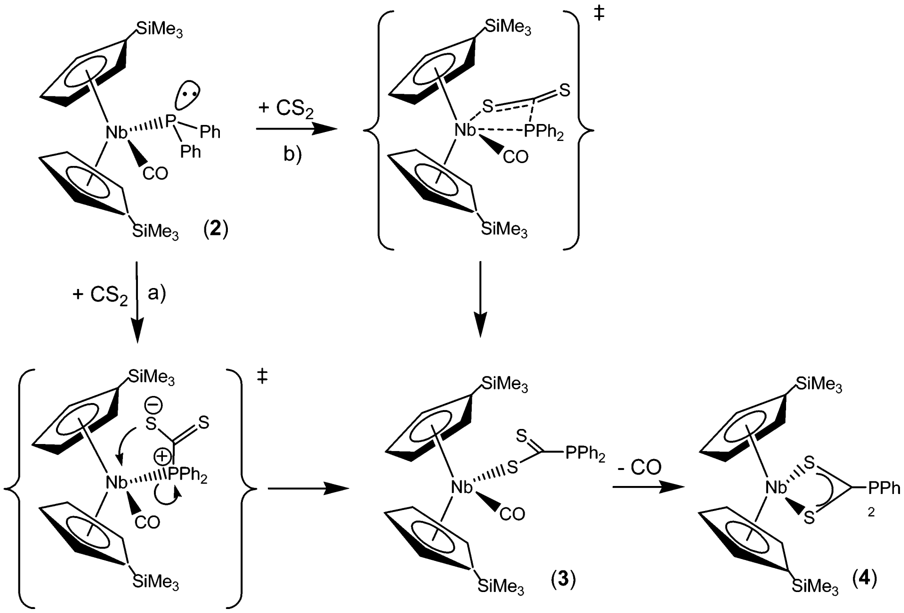
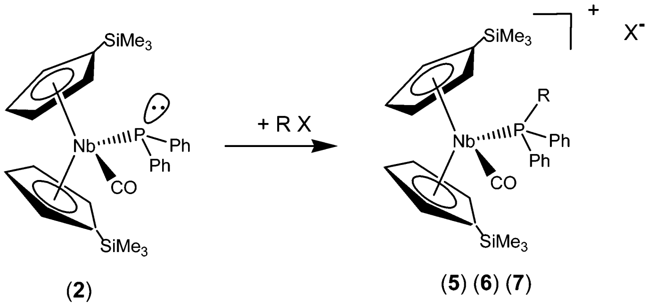
Scheme 2



Scheme 3



complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(CO)]X$ (R = Me, X = I (**5**); CH_2Ph, X = Br (**6**); CH_2CH_2Ph X = Br (**7**)) in high yield (see eq 2):

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]\ (\mathbf{2}) \xrightarrow{+RX} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PRPh_2)(CO)]X \quad (2)$$

R = Me X = I (**5**)
R = $PhCH_2$ X = Br (**6**)
R = $PhCH_2CH_2$ X = Br (**7**)

The formation of these complexes must be considered, in terms of an alkylation process, as the result of electrophilic attack of the alkyl halide on the nucleophilic P atom of the phosphido terminal ligand[7a] (see Scheme 3).

Complexes **5**, **6**, and **7** were isolated as deep red air-sensitive crystalline solids. The low solubility of the complexes in hydrocarbons, ethers, and aromatic solvents enabled us to isolate the products very easily in analytically pure form. Fortunately, all of the complexes are sufficiently soluble in acetone to allow their NMR spectra to be recorded. The ionic nature of complexes **5**, **6**, and **7** was confirmed by measurement of the molar conductivity (Λ_M = 126.8, 166.6, and 134.7 Ω^{-1} cm^2 mol^{-1} for **5**, **6**, and **7**, respectively), and the values are consistent with 1:1 electrolytes.[11]

Compounds **5**, **6**, and **7** were characterized spectroscopically (see Experimental Section). The most significant bands in the IR spectra appear at 1968, 1947, and 1911 cm^{-1}, which correspond to ν(CO) for **5**, **6**, and **7**, respectively. The ^{31}P NMR spectra each show a broad resonance, and these appear at δ 45.4, 55.7, and 48.4 for **5**, **6**, and **7**, respectively. These chemical shift values show the effect of alkylation of the phosphorus by comparison with the ^{31}P NMR chemical shift of the phosphido terminal ligand in complex **2**. This comparison shows the differences in electron density on the P atom. In agreement with the IR spectra, the $^{13}C\{^1H\}$ NMR spectra of **5**−**7** show low-field resonances for the carbonyl ligand (ca. δ 250 ppm) as broad signals due to the quadrupolar moment of the niobium atom.

The use of 1,2-diiodoethane (ICH_2CH_2I) as the alkylating reagent with **2** gave the unexpected cationic iodophosphinonioboocene triiodide complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CO)]I_3$ (**8**) rather than the expected dicationic derivative $[\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CO)\}_2(Ph_2P(CH_2CH_2)PPh_2)]I_2$ (see eq 3).

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]\ (\mathbf{2}) \xrightarrow[-\ CH_2=CH_2]{+\ I\text{-}CH_2\text{-}CH_2\text{-}I} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CO)]I_3\ (\mathbf{8}) \quad (3)$$

The reaction of complex **2** with I_2/Et_2O was successful as an alternative method to obtain derivative **8**. The new iododiphenylphosphine complex was isolated as a deep red air-sensitive solid. The ionic nature of complex **8** was confirmed by measurement of the molar conductivity (Λ_M = 146.7 Ω^{-1} cm^2 mol^{-1}), which is consistent with a 1:1 electrolyte.[11] The structural characterization was carried out by both spectroscopic and X-ray diffraction studies (see Experimental Section).

The IR spectrum shows one band at 1969 cm^{-1}, and this corresponds to ν(CO). In the NMR spectra (^{1}H and ^{13}C) the absence of a resonance in the typical region for the $Ph_2P(CH_2CH_2)PPh_2$ ligand, corresponding to the ethylene bridge of the $P(CH_2CH_2)P$ moiety, confirms that this ligand is not present. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance of the CO ligand at δ 210 ppm. The ^{31}P NMR spectrum contains a signal at δ 40.0 ppm due to the iodophosphine ligand. These chemical shift values show the effect of the presence of the iodine atom by comparison with the data for complex **2**. This comparison is consistent with the decreasing electronic density.

X-ray Diffraction Study of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(P(I)Ph_2)(CO)]I_3$ (8). A microcrystalline sample of **8** suitable for X-ray diffraction was obtained by recrystallization from CH_2Cl_2/Et_2O.

The ORTEP diagram of **8** is shown in Figure 3. Selected bond distances and bond angles are listed in Table 1.

Complex **8** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit cell. The local coordina-

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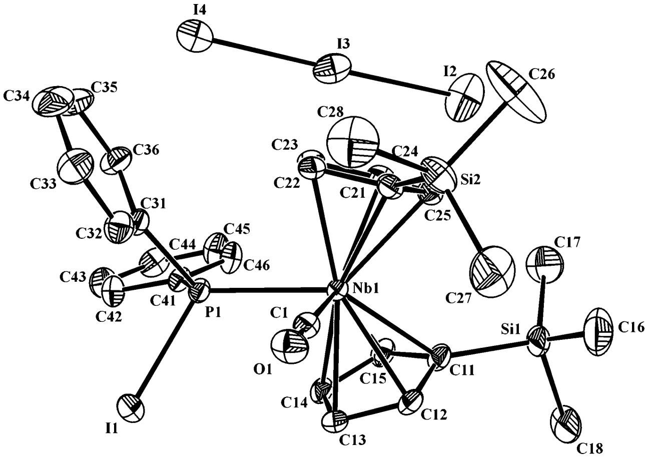

Figure 3. Molecular structure of **8** with 30% probability ellipsoids. Hydrogen atoms have been omitted.

tion geometry around the Nb atom can be described as pseudo-tetrahedral with two cyclopentadienyl rings bonded to the metal in a η^5-mode and phosphorus and carbon atoms of the iodophosphine and carbonyl ligands, respectively, comprising the immediate coordination sphere. The distances between the metal atom and the centroids of the Cp rings are 2.062(6) and 2.054(5) Å, and the value of the angle Cent(1)−Nb(1)−Cent(2) is 141° (Cent(1) is the centroid of C(11)−C(15) and Cent(2) is the centroid of C(21)−C(25)). These values are typical of bent niobocene derivatives. The Nb(1)−P(1) bond distance is 2.542(5) Å, and this is in the usual range found for phosphinoniobocene derivatives.[12]

The I(1)−P(1) bond length of 2.472(1) Å is close to the values of 2.43(4) and 2.398(3) Å found in PI_3 and $[Ph_3PI]I_3$, respectively.[13,14] The carbonyl ligand has a typical terminal CO disposition in agreement with the bond distance and angle values of Nb(1)−C(1), C(1)−O(1), and Nb(1)−C(1)−O(1), which are 2.067(6) Å, 1.132(8) Å, and 178.3(6)°, respectively. The P atom is pseudo-tetrahedral. As far as the triiodide anion is concerned, the bond distances between I(2)−I(3) and I(3)−I(4) are practically equivalent, with values of 2.921(2) and 2.924(1) Å, and the value of I(2)−I(3)−I(4) is 177.39(3)°, in agreement with a linear disposition.

Although there are numerous reports in the literature on the structures of triiodide compounds,[14] compound **8** appears to be unique in two ways. First, it is the only complex to include an iodophosphino-metallocene cation, and second, it is the only example in which a PIR_2 ligand is coordinated to an early transition metal that has been characterized by X-ray diffraction.

The preparation of complex **8** could proceed according to the four steps depicted in Scheme 4. Step 1 corresponds to the electrophilic attack on the phosphorus atom followed by the elimination of $CH_2{=}CH_2$ and iodine, step 2. The subsequent attack by the iodine, steps 3 and 4, would give the final complex **8**. Steps 3 and 4 were experimentally confirmed since the direct reaction of **2** with I_2 gave **8** and are consistent with the mechanism reported by Cotton et al.[15] for the formation of $[Ph_3PI]I_3$ on employing Ph_3P and I_2.

Conclusions

We have studied the reactivity of a phosphido-containing niobocene complex **2** toward CS_2, and an insertion process into the Nb−P bond occurs to give complexes **3** and **4**, where a phosphinodithioformato ligand is present. The X-ray molecular structure of **3** has been carried out, and it represents the first example of an early transition metal where a phosphinodithioformato ligand has a κ^1-S coordination mode. Additionally, the electrophilic attack of alkyl halides on the phosphorus atom of the phosphide ligand in **2** has allowed the isolation of a new family of d^2 cationic niobocene species **5**−**7**. Finally, an interesting reactivity was found in the reaction of **2** with ICH_2CH_2I, yielding the complex **8**, whose X-ray crystal structure has also been determined.

Experimental Section

General Procedures. All reactions were carried out using Schlenk techniques. Oxygen and water were excluded through the use of vacuum lines supplied with purified N_2. Toluene was distilled from sodium. Hexane was distilled from sodium/potassium alloy. Diethyl ether and THF were distilled from sodium benzophenone. All solvents were deoxygenated prior to use. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2)CO)]Cl$ (**1**)[6] was prepared as described in the literature. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use. $ClPPh_2$, CS_2, MeI, $(C_6H_5)CH_2Br$, $(C_6H_5)CH_2CH_2Br$, and I_2 were used as supplied by Aldrich. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Innova 500 MHz spectrometer at ambient temperature unless stated otherwise. ^1H, ^{13}C, and ^{31}P NMR chemical shifts (δ values) are given in ppm relative to the solvent signal (^1H, ^{13}C) or standard resonances (^{31}P, external 85% H_3PO_4). IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as Nujol mulls on CsI windows.

Synthesis of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]$ (2). A solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PHPh_2(CO))]Cl$ (**1**) (0.56 g, 0.87 mmol) in toluene (30 mL) was treated with 0.5 M aqueous NaOH (1.72 mL, 10% excess). The mixture was vigorously stirred. Within 4 h the precipitate had dissolved and the organic phase had turned dark brown. The toluene solution was filtered and evaporated to dryness. The product **2** was obtained as a yellow-brown oil in 80% yield. IR (Nujol): ν (cm^{-1}) 1918 (CO). ^1H NMR (500 MHz, C_6D_6): δ 0.22 (s, 18 H, Si*Me*$_3$), 4.33, 4.74, 4.80, 5.30 (m, 2 H each a complex signal, C_5*H*$_4$SiMe$_3$); 7.15, 7.23, 7.26 (m, C_6*H*$_5$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 0.1 (Si*Me*$_3$), 97.0 (C^1, *C*$_5$H$_4$SiMe$_3$), 93.9, 95.3, 98.9, 102.6 (C^{2-5}, exact assignment not possible, *C*$_5$H$_4$SiMe$_3$); 124.4 (*C*$_6$H$_5$), 133.0, 134.1 (d, $^2J_{CP}$ = 17.00 Hz, *C*$_6$H$_5$), 150.9 (d, $^1J_{CP}$ = 35.18 Hz, *C*$_6$H$_5$), 253.2 (*C*O). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ −10.8 (*P*Ph$_2$). Anal. Calcd for $C_{31}H_{36}NbOPSi_2$: C, 61.60; H, 6.00. Found: C, 61.10; H, 5.90.

Synthesis of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\kappa^1\text{-}SC(S)(PPh_2))(CO)]$ (3). Compound $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PPh_2)(CO)]$ (**2**) (0.56 g, 0.93 mmol) was treated with a stoichiometric amount of CS_2 (0.07 g, 0.06 mL, ρ = 1.26 g/mL; 0.93 mmol), and the mixture was stirred with dry THF (30 mL) at room temperature for 4 h. During this time the solution changed color from yellow-brown to dark red. The solvent was evaporated under vacuum to dryness. The dark red oily residue was extracted with hexane (5 mL). The resulting solution was filtered and evaporated to dryness. The deep red oil was dissolved in hexane (5 mL) and kept at 5 °C for 10 h. A

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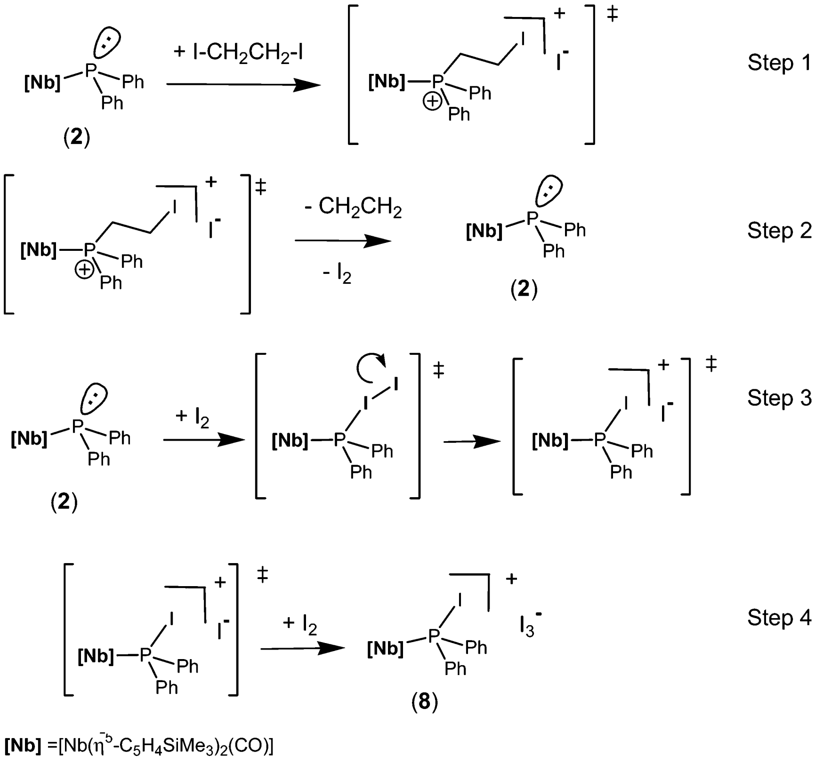
Scheme 4



microcrystalline dark purple-red solid was obtained. The solid was filtered off to give 80% yield of **3**. IR (Nujol): ν (cm^{-1}) 1927 (CO), 1046 (C=S), 634 (C−S). ^{1}H NMR (500 MHz, C_6D_6): δ 0.01 (s, 18 H, Si*Me*$_3$), 4.71 (4 H, a complex signal, C_5*H*$_4$SiMe$_3$) 4.92, 5.33 (2 H, each a complex signal, C_5*H*$_4$SiMe$_3$); 7.00−7.54 (10 H, C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.1 (Si*Me*$_3$), 97.0 (C^1, *C*$_5$H$_4$-SiMe$_3$), 94.1, 95.6, 99.1 (C$^{2-5}$, exact assignment not possible, *C*$_5$H$_4$-SiMe$_3$); 127.7, 127.8, 133.4 (*C*$_6$H$_5$) (d, $^2J_{CP}$ = 16.70 Hz, *C*$_6$H$_5$), 150.9, 151.0 (d, $^1J_{CP}$ = 25.30 Hz, *C*$_6$H$_5$); 254.6 (*C*O). 264.0 (d, $^1J_{CP}$ = 47.62 Hz, *C*S$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 46.9 (*P*Ph$_2$). Anal. Calcd for $C_{32}H_{36}NbOPS_2Si_2$: C, 56.48; H, 5.33. Found: C, 56.03; H, 5.21.

Synthesis of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(κ^2-S,S-SC(S)(PPh$_2$))] (4). A mixture of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(κ^1-S-SC(S)(PPh$_2$))(CO)] (**3**) (0.56 g, 0.82 mmol) and dry THF (20 mL) was stirred at room temperature for 8 h. During this time the solution changed color from dark red to dark green. The solvent was evaporated under vacuum to dryness. The dark green oily residue was extracted with hexane (5 mL). The solid was filtered off to give 90% yield of **4**. IR (Nujol): ν (cm^{-1}) 1000 (*C*=*S*). ^{1}H NMR (500 MHz, C_6D_6): δ 0.23 (s, 18 H, Si*Me*$_3$), 4.94, 5.09 (m, 4 H each a complex signal, C_5*H*$_4$SiMe$_3$); 6.55 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, C_6*H*$_5$), 6.80 (d, $^3J_{HH}$ = 7.1 Hz, 4 H, C_6*H*$_5$), 7.53 (t, $^3J_{HH}$ = 7.1 Hz, 4 H, C_6*H*$_5$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.4 (Si*Me*$_3$), 105.9 (C^1, *C*$_5$H$_4$SiMe$_3$), 97.8, 105.3 (C$^{2-3}$, exact assignment not possible, *C*$_5$H$_4$SiMe$_3$); 124.3, 125.7, 129.7 (*C*$_6$H$_5$), 141.8 (d, $^1J_{CP}$ = 23.00 Hz, *C*$_6$H$_5$), 244.0 (d, $^1J_{CP}$ = 20.00 Hz, *C*S$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 2.03 (*P*Ph$_2$). $_{31}$P{^{1}H} NMR (202 MHz, C_6D_6): δ 2.03 (q, $^3J_{PH}$ = 7.30 Hz, PPh$_2$). Anal. Calcd for $C_{31}H_{36}NbPS_2Si_2$: C, 56.80; H, 5.54. Found: C, 56.00; H, 5.33.

Syntheses of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(PRPh$_2$)(CO)], R = CH$_3$ (5); R = CH$_2$C$_6$H$_5$ (6); R = CH$_2$CH$_2$C$_6$H$_5$ (7). To a solution of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(PPh$_2$)(CO)] (**2**) (0.50 g, 0.83 mmol) in dry toluene (30 mL) was added an excess of the appropriate alkyl halide (**5**, methyl iodide (1:10) (1.17 g, 0.51 mL, ρ = 2.28 g/mL, 8.30 mmol); **6**, benzyl bromide (1:10) (1.42 g, 0.98 mL, ρ = 1.44 g/mL, 8.30 mmol); and **7** 1-bromo-2-ethylbenzene (1:10) (1.53 g, 1.14 mL, ρ = 1.34 g/mL, 8.30 mmol)). In each case the reaction mixture was stirred at room temperature for 2 h. During this time the solution changed to a deep red color. The solvent was evaporated under vacuum to dryness. The resulting solid was recrystallized by dissolving it in dichloromethane and placing a layer of diethyl ether above it in a Schlenk tube. Deep red crystals began to grow within a few days. The resulting solid was filtered off to give a deep red solid in 80%, 85%, and 80% yield for **5**, **6**, and **7**, respectively.

Complex 5. IR (Nujol): ν (cm^{-1}) 1968 (CO). ^{1}H NMR (500 MHz, C_6D_6): δ 0.05 (s, 18 H, Si*Me*$_3$), 2.92 (d, $^2J_{HP}$ = 14.8 Hz, C*H*$_3$), 5.06, 5.49, 5.73, 5.88 (2 H each a complex signal, C_5*H*$_4$-SiMe$_3$); 7.82 (m, 10 H, C_6*H*$_5$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 0.8 (Si*Me*$_3$); 20.5 (d, $^1J_{CP}$ = 30.65 Hz, *C*H$_3$), 95.5 (C^1, *C*$_5$H$_4$-SiMe$_3$), 96.9, 97.3, 101.5, 102.2 (C$^{2-5}$, exact assignment not possible, *C*$_5$H$_4$SiMe$_3$); 130.2 (d, $^3J_{CP}$ = 9.70 Hz, *C*$_6$H$_5$), 131.8 (*C*$_6$H$_5$), 132.9 (d, $^2J_{CP}$ = 10.20 Hz, *C*$_6$H$_5$), 136.5 (d, $^1J_{CP}$ = 39.79 Hz, *C*$_6$H$_5$); 250.0 (*C*O). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 45.4 (s, *P*MePh$_2$). Anal. Calcd for $C_{32}H_{39}INbOPSi_2$: C, 51.49; H, 5.26. Found: C, 51.18; H, 5.15.

Complex 6. IR (Nujol): ν (cm^{-1}) 1947 (CO). ^{1}H NMR (500 MHz, C_6D_6): δ 0.31 (s, 18 H, Si*Me*$_3$); 4.01 (d, 2 H, $^2J_{HP}$ = 4.4 Hz, C*H*$_2$(C$_6$H$_5$)); 5.14, 5.56, 5.85, 5.93 (2 H each a complex signal, C_5*H*$_4$SiMe$_3$); 7.21 (m, 15 H, C_6*H*$_5$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ −0.2 (Si*Me*$_3$), 35.6 (d, $^1J_{CP}$ = 15.30 Hz, *C*H$_2$(C$_6$H$_5$); 94.4, 98.83, 99.1, 100.8 (C$^{2-5}$, exact assignment not possible, *C*$_5$H$_4$-SiMe$_3$); 103.1 (C^1 from *C*$_5$H$_4$), 125.5−133.3 (m, *C*$_6$H$_5$); 250.0 (*C*O). ^{31}P{^{1}H} NMR (125 MHz, C_6D_6): δ 55.8 (s, *P*(CH$_2$(C$_6$H$_5$))(C$_6$H$_5$)$_2$). Anal. Calcd for $C_{38}H_{43}BrNbOPSi_2$: C, 58.86; H, 5.59. Found: C, 58.99; H, 5.73.

Complex 7. IR (Nujol): ν (cm^{-1}) 1911 (CO). ^{1}H NMR (500 MHz, C_6D_6): δ 0.24 (s, 18 H, Si*Me*$_3$), 2.67 (m, 2 H, CH$_2$C*H*$_2$Ph), 2.90 (m, 2 H, C*H*$_2$CH$_2$Ph), 5.22, 5.56, 5.75, 5.83 (2 H each a complex signal, C_5*H*$_4$SiMe$_3$); 7.21 (m, 15 H, C_6*H*$_5$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ −0.6 (Si*Me*$_3$), 31.2 (d, $^2J_{CP}$ = 6.00 Hz, CH$_2$*C*H$_2$Ph), 34.0 (d, $^1J_{CP}$ = 20.00 Hz, *C*H$_2$CH$_2$Ph), 94.9, 96.9, 100.8, 102.0 (C$^{2-5}$, exact assignment not possible, *C*$_5$H$_4$SiMe$_3$); 104.0 (C^1, *C*$_5$H$_4$SiMe$_3$), 130.2, 131.8, 132.9 (*C*$_6$H$_5$), 136.5 (d, $^1J_{CP}$ = 39.79 Hz, *C*$_6$H$_5$); 250.0 (*C*O). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6):

δ 48.2 (s, *P*(CH_2CH_2Ph)Ph_2). Anal. Calcd for $C_{39}H_{45}BrNbOPSi_2$: C, 59.34; H, 5.75. Found: C, 59.55; H, 5.84.

Synthesis of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(P(I)Ph_2)(CO)]I_3 (8). Method 1. To a solution of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(PPh_2)(CO)] (**2**) (0.45 g, 0.74 mmol) in dry toluene (30 mL) was added excess 1,2-diiodoethane (ICH_2CH_2I (1:10) (2.23 g; 1.05 mL; ρ = 2.13 g/mL; 7.40 mmol)). The reaction mixture was stirred at room temperature for 2 h. During this time the solution changed to a deep red color. The solvent was evaporated under vacuum to dryness. The remaining solid was crystallized by dissolving it in dichloromethane and placing a layer of diethyl ether above it in a Schlenk tube. Deep red crystals began to grow within a few days. The resulting solid was filtered off to give a deep red solid in 85% yield.

Method 2. To a solution of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(PPh_2)(CO)] (**2**)-(0.50 g, 0.83 mmol) in dry toluene (30 mL) was added excess I_2 in diethyl ether (1:2) (0.42 g; 1.66 mmol). The reaction mixture was stirred at room temperature for 2 h. During this time the solution changed to a deep red color. The solvent was evaporated under vacuum to dryness. The resulting solid was crystallized by dissolving it in dichloromethane and placing a layer of diethyl ether above it in a Schlenk tube. Deep red crystals began to grow within a few days. The resulting solid was filtered off to give a deep red solid in 80% yield.

Complex 8. IR (Nujol): ν (cm^{-1}) 1969 (CO). ^{1}H NMR (500 MHz, C_6D_6): δ 0.34 (s, 18 H, Si*Me*$_3$); 5.25, 5.31, 5.69, 6.08 (2 H each a complex signal, C_5*H*$_4$SiMe$_3$); 7.75 (m, 10 H, C_6*H*$_5$). ^{13}C-{^{1}H} NMR (125 MHz, C_6D_6): δ −0.1 (Si*Me*$_3$), 97.4, 100.9, 102.8, 103.8 (C$^{2-5}$, exact assignment not possible, *C*$_5$H$_4$SiMe$_3$); 107.1 (C^1, *C*$_5$H$_4$SiMe$_3$); 129.9 133.1 134.1 (*C*$_6$H$_5$); 135.6 (d, $^1J_{CP}$ = 25.30 Hz, *C*$_6$H$_5$); 210.0 (*C*O). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 40.0 (s, *P*IPh_2). Anal. Calcd for $C_{31}H_{36}I_4NbOPSi_2$: C, 33.48; H, 3.26. Found: C, 33.35; H, 3.21.

X-ray Structure Determination of 3 and 8. Crystal data collection and refinement parameters are collected in Table 2. Suitable crystals were selected and mounted on a fine glass fiber with epoxy cement, sealed, and used for data collection. The unit cell parameters were determined from the angular setting of a least-squares fit of 25 strong high-angle reflections. Reflections were collected at 250 K (for **3**) and 230 K (for **8**) on a NONIUS-MACH3 diffractometer equipped with graphite-monochromated radiation (λ = 0.71073 Å). The samples did not show significant intensity decay during data collection.

Data were corrected in the usual fashion for Lorentz and polarization effects, and a semiempirical absorption correction[16] was applied (μ = 37.56 cm^{-1} (**3**) and 6.46 cm^{-1} (**8**)). The space group was determined from the systematic absences in the diffraction data. The structures were solved by direct methods,[17] and refinement on F^2 was carried out by full-matrix least-squares analysis.[18] Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions but not refined.

Table 2. Crystal Data and Structure Refinement for 3 and 8

	3	8
empirical formula	$C_{30}H_{36}NbOPS_2Si_2$	$C_{29}H_{36}I_4NbOPSi_2$
fw	656.77	1088.24
temperature (K)	250(2)	230(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	17.063(8)	11.608(1)
b (Å)	10.834(8)	12.194(5)
c (Å)	18.488(6)	14.197(2)
α (deg)		81.77(2)
β (deg)	108.76(4)	78.42(1)
γ (deg)		72.22(1)
volume (Å^3)	3236(3)	1867.4(8)
Z	4	2
density (calcd) (g/cm^3)	1.348	1.935
abs coeff (cm^{-1})	6.46	37.56
range of transmn factor	0.689−1.000	0.591−1.000
F(000)	1360	1028
cryst size (mm^3)	0.4 × 0.3 × 0.3	0.3 × 0.3 × 0.2
index ranges	$-19 \le h \le 18$	$-15 \le h \le 15$
	$0 \le k \le 12$	$-15 \le k \le 16$
	$0 \le l \le 20$	$0 \le l \le 18$
no. of indep reflns	4874/4700 [*R*(int) = 0.0914]	8989 [*R*(int) = 0.0218]
no. of data/restraints/params	4700/0/334	8989/0/343
goodness-of-fit on F^2	0.958	1.027
final *R* indices [$I > 2\sigma(I)$]^a	R1 = 0.0863, wR2 = 0.1398	R1 = 0.0548, wR2 = 0.1484
largest diff peak and hole (e·Å^{-3})	0.747 and −0.671	4.118 and −4.117

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

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Supporting Information Available: Detailed X-ray crystallographic data of atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for complexes **3** and **8**. Tables of X-ray crystallographic data for complexes **3** and **8**. This material is available free charge of charge via the Internet at http://pubs.acs.org.

OM051013U

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