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# Reactivity of $[N(CH_2CH_2PPh_2)_3]CoH$ toward $CS_2$ , $SCNPh$ , $OCNPh$ , and $COS$

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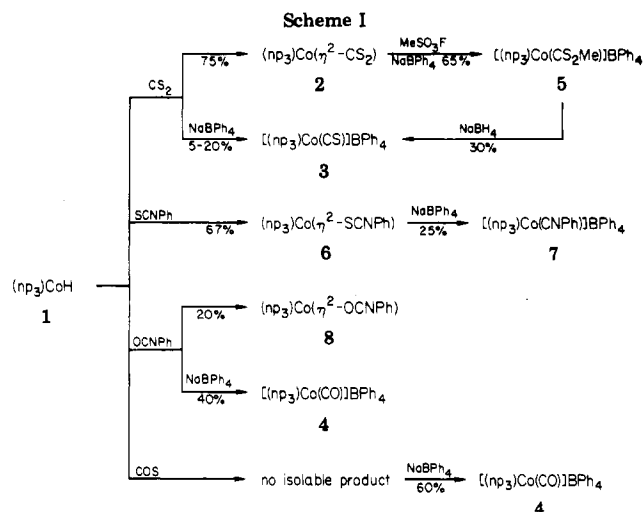
Reaction of  $(np_3)CoH$  (1) [ $np_3$  = tris[2-(diphenylphosphino)ethyl]amine] with  $CS_2$ ,  $SCNPh$ , or  $OCNPh$  affords  $(np_3)Co(\eta^2-CS_2)$  (2),  $(np_3)Co(\eta^2-SCNPh)$  (6), and  $(np_3)Co(\eta^2-OCNPh)$  (8), respectively. In the presence of  $NaBPh_4$  1 reacts with  $CS_2$  or  $SCNPh$  to give  $[(np_3)Co(CS)]BPh_4$  (3) and  $[(np_3)Co(CNPh)]BPh_4$  (7), respectively, and with  $OCNPh$  or  $COS$  to give  $[(np_3)Co(CO)]BPh_4$  (4). Methylation of 2 by  $MeSO_3F$ , followed by  $NaBPh_4$  addition, leads to  $[Ph_2PCH_2CH_2N(CH_2CH_2PPh_2)_2Co(CS_2Me)]BPh_4$  (5) through intramolecular attack by a phosphorus atom of  $np_3$  on a formed in situ  $\eta^2$ -dithiomethyl ester group. On reaction of 5 with  $NaBH_4$  the  $P-CS_2Me$  and  $C-SMe$  bonds are cleaved and the thiocarbonyl complex 3 is formed.

## Introduction

In recent years the reactivity of heteroallenes of formula  $X=C=Y$  ( $X, Y = O, S, NR, CR_2$ ) toward transition-metal complexes has been intensively investigated.<sup>1</sup> Although the results obtained have more often demonstrated the diversity of the individual chemistries of these molecules rather than their reciprocal use as "equivalent molecules" and "model compounds", still these heterocumulenes have some chemical properties in common. One of these is the side-on coordination to metals by one of the double bonds. This mode of coordination is fairly easily realized for the  $C=S$  fragment of the heterocumulene but relatively rare for  $C=N$  and  $C=O$  fragments.

It appears quite evident from a perusal of the literature that the stabilization of  $\eta^2$ -heteroallene complexes is dependent on a number of factors: one of these is surely the nature of the heteroallene itself. Another factor of critical importance is the total electron count of the fragment formed by the metal and the other coligands. In fact, as it has been pointed out,<sup>2</sup> the fragment must fulfill certain electronic requirements to stabilize the  $\eta^2$  mode; at the same time the geometry of the fragment, which is somewhat dependent on the nature of the coligands, plays a critical role. Finally when all of the above conditions are even, the nature of the metal itself may generate a differential chemical behavior.

Experimentally all of these points are substantiated by the following examples. Carbon dioxide forms the complex  $(PCy_3)_2Ni(\eta^2-CO_2)$ ,<sup>3</sup> whereas carbon disulfide forms the dimer  $[(PCy_3)Ni(\mu-CS_2)]_2$ ,<sup>4</sup> under the same conditions organo isocyanates and isothiocyanates do not give any stable  $\eta^2$ -heteroallene complexes. Formation of an ( $\eta^2$ -isocyanate)nickel complex, namely,  $(PPh_3)_2Ni(\eta^2-PhNCO)$ ,



needs triphenylphosphine as an ancillary ligand,<sup>5</sup> and the only nickel complexes containing  $\eta^2-CS_2$ <sup>6</sup> and  $SCNPh$ <sup>7</sup> groups exist with the tripodlike tris(tertiary phosphine) 1,1,1-tris[(diphenylphosphino)methyl]ethane (triphos). On the other hand, the instability of complexes of formula  $(PR_3)_2M(\eta^2-CS_2)$  cannot be considered indeed typical of  $d^{10}$  metals since the first  $\eta^2-CS_2$  complex that has been synthesized is  $(PPh_3)_2Pt(\eta^2-CS_2)$ .<sup>8</sup>

We were intrigued by the possibility of finding a metal-ligand moiety capable of forming stable  $\eta^2$  complexes with a major number of heteroallenes. Our choice fell on the  $(np_3)Co$  moiety [ $np_3$  = tris[2-(diphenylphosphino)ethyl]amine] which has the following peculiarities:<sup>9</sup> (i) the  $(np_3)Co$  fragment has a limited number of orbitals available for interaction with the molecule to be activated; (ii) it is unlikely that the  $np_3$  ligand is displaced from the metal even under strong reaction conditions; (iii) the presence of six phenyl rings attached to the phosphorus atoms provides a conspicuous shield to a coordinated group, thus preventing condensation reactions. As a source of the  $(np_3)Co$  unit we have exploited the complex  $(np_3)CoH$  (1)

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which is known to undergo facile substitutions of the hydridic hydrogen atom with neutral groups.<sup>9</sup>

Here we report the reactions of complex **1** with carbon disulfide, phenyl isothiocyanate, phenyl isocyanate, and carbonyl sulfide (Scheme I).

### Experimental Section

Compound **1** was prepared according to a published procedure.<sup>9</sup> Reagent grade chemicals were used in the preparation of the complexes. Tetrahydrofuran (THF) was purified by distillation over  $LiAlH_4$  just before use. *n*-Butyl ether and *n*-pentane were distilled over sodium and stored under nitrogen. All operations were routinely performed under nitrogen by using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using samples mullied in Nujol between KBr plates. <sup>31</sup>P NMR spectra of  $CDCl_3$  solutions were taken on a Varian CFT 20 spectrometer. Chemical shifts are downfield (+) from external  $H_3PO_4$ . Ultraviolet-visible spectra were recorded on a Beckman DK-2A spectrophotometer. Magnetic susceptibilities of solid samples were measured on a Faraday balance. Conductance measurements were made by using a WTW Model LBR/B conductivity bridge in ca.  $10^{-3}$  M nitroethane solutions.

**Syntheses.**  $(np_3)Co(\eta^2-CS_2)$  (**2**). Carbon disulfide vapors were bubbled for 5 min through a suspension of **1** (1.3 g, 1.8 mmol) in THF (130 mL); during this time the color changed from red-orange to red-brown. By addition of ethanol (90 mL) red-brown crystals separated, which were collected and washed with ethanol and petroleum ether; yield 75%. Anal. Calcd for  $C_{43}H_{42}CoNP_3S_2$ : C, 65.47; H, 5.36; Co, 7.47; N, 1.77; S, 8.12. Found: C, 65.17; H, 5.42; Co, 7.35; N, 1.67; S, 8.16.

On concentration of the filtrate and addition of solid  $NaBPh_4$  (0.3 g) red crystals of  $[(np_3)Co(CS)]BPh_4$  (**3**) were formed; yield 5%.

$[(np_3)Co(CS)]BPh_4$  (**3**). **Method 1.** A large excess of carbon disulfide (10 mL) was added to a suspension of **1** (0.71 g, 1 mmol) in THF (50 mL). The resultant mixture was stirred for 10 h, and then  $NaBPh_4$  (0.51 g, 1.5 mmol) in *n*-butanol (60 mL) was added. The compound crystallized as red crystals on standing; these were filtered and washed with ethanol and petroleum ether; yield 20%.

**Method 2.** A hot suspension of **5** (0.43 g, 0.38 mmol) in THF (100 mL) was treated under stirring with a large excess of  $NaBH_4$  (0.06 g, 1.6 mmol) in ethanol (20 mL). The resultant solution was left standing overnight and then concentrated to 20 mL. The red crystals that formed were collected and washed as above; yield 30%. Anal. Calcd for  $C_{67}H_{62}BCoNP_3S$ : C, 74.79; H, 5.8; Co, 5.47; N, 1.3; S, 2.97. Found: C, 74.71; H, 5.73; Co, 5.38; N, 1.22; S, 3.02.

$[(np_3)Co(CS_2Me)]BPh_4$  (**5**). A hot suspension of **2** (0.55 g, 0.7 mmol) in THF (40 mL) was treated with neat  $MeSO_3F$  (0.07 mL, 0.85 mmol) which caused the solid to dissolve to give a deep brown solution. Addition of  $NaBPh_4$  (0.34 g, 1 mmol) in ethanol (30 mL) precipitated brown crystals that were filtered and washed with ethanol and petroleum ether; yield 65%. Anal. Calcd for  $C_{68}H_{65}BCoNP_3S_2$ : C, 72.72; H, 5.83; Co, 5.24; N, 1.24; S, 5.70. Found: C, 72.63; H, 5.79; Co, 5.21; N, 1.19; S, 5.62.

$(np_3)Co(\eta^2-SCNPh)$  (**6**). Neat SCNPh (0.2 mL, 1.7 mmol) was added to a magnetically stirred suspension of **1** (1 g, 1.4 mmol) in THF (25 mL). After 15 min the resulting deep red solution was treated with a 4:1 mixture of *n*-butyl ether and ethanol (50 mL), giving brick red crystals that were collected and washed with *n*-butyl ether and *n*-pentane; yield 67%. Anal. Calcd for  $C_{48}H_{47}CoN_2P_3S$ : C, 69.41; H, 5.58; Co, 6.95; N, 3.3; S, 3.78. Found: C, 69.28; H, 5.51; Co, 6.92; N, 3.28; S, 3.81.

$[(np_3)Co(CNPh)]BPh_4$  (**7**). A mixture of **6** (0.3 g, 0.35 mmol) and  $NaBPh_4$  (0.13 g, 0.4 mmol) in  $CH_2Cl_2$  (30 mL) and ethanol (10 mL) was magnetically stirred for 14 h. On concentration the product precipitated as red solid that was filtered and washed with ethanol and petroleum ether; yield 25%. Anal. Calcd for  $C_{73}H_{67}BCoN_2P_3$ : C, 77.24; H, 5.95; Co, 5.19; N, 2.46. Found: C, 77.02; H, 6.03; Co, 5.04; N, 2.38.

$(np_3)Co(\eta^2-OCNPh)$  (**8**). A suspension of **1** (0.71 g, 1 mmol) in THF (20 mL) was treated at 0 °C with neat OCNPh (0.12 mL, 1.1 mmol). After 30 min the resultant red orange solution was reduced to half volume. Addition of pentane (10 mL) precipitated

in few minutes orange crystals that were quickly filtered and washed with *n*-pentane; yield 20%. Owing to the high instability of this compound repeated analyses did not give homogeneous results. However, the Co:N ratio is approximately 1:2. Addition of  $NaBPh_4$  (0.3 g) in ethanol to the filtrate afforded red crystals of  $[(np_3)Co(CO)]BPh_4$ <sup>17</sup> (**4**); yield 40%.

**Reaction of 1 with COS.** Carbonyl sulfide was bubbled for 15 min through a THF (20 mL) suspension of **1** (0.71 g, 1 mmol) giving an orange-brown solution. Addition of  $NaBPh_4$  (0.38 g, 1.1 mmol) in *n*-butanol (20 mL) precipitated red crystals of **4** that were filtered and washed with ethanol and petroleum ether; yield 60%.

### Results and Discussion

**Reaction with Carbon Disulfide.** A tetrahydrofuran solution of **1** reacts at room temperature with  $CS_2$  producing a red-brown solution. Addition of ethanol precipitates, in good yield, red-brown crystals of empirical formula  $(np_3)Co(CS_2)$  (**2**). **2** is fairly air stable in the solid state but rather unstable in solution. It is sparingly soluble in chlorinated solvents; unfortunately the concentrations are low so as to preclude any characterization in solution. The room-temperature  $\mu_{eff}$  is equal to 2.20  $\mu_B$ , corresponding to a doublet ground state. The reflectance spectrum, with absorption maxima at 6700, 11 250, 16 400 (sh), and 21 750  $cm^{-1}$ , is comparable with those of distorted square-pyramidal Co(0) complexes<sup>10</sup> as well as with those of square-pyramidal low-spin Co(II) complexes.<sup>9</sup> In regard to this, it should be pointed out that the formation of  $\eta^2-CS_2$  metal complexes can be considered as an oxidative reaction, and thus the complexes may be regarded formally as containing the metals with oxidation numbers increased by two units. Hence, it is not surprising that the electronic spectra are often more compatible with the oxidized formulation. The IR spectrum contains no  $\nu(Co-H)$  vibrations but there are two bands at 1125 and 630  $cm^{-1}$  which, by comparison with the IR spectra of the complexes  $(triphos)M(\eta^2-CS_2)$  ( $M = Co, Ni$ ),<sup>6,10</sup> have been assigned to the out-of-ring  $\nu(C=S)$  and to the in-ring  $\nu(C-S)$  stretching vibrations, respectively. The IR spectrum also exhibits a band at 2800  $cm^{-1}$  which is not present in the IR spectrum of the starting product **1**. From a perusal of IR data and crystal structures of a variety of  $np_3$  metal complexes, we have ascertained that an infrared band at 2800  $cm^{-1}$  appears whenever the nitrogen atom of  $np_3$  is not coordinated to the metal, that is the  $np_3$  ligand acts as a tridentate ligand. The stretching frequencies of  $CH_2$  groups are in the region 2890–2850  $cm^{-1}$ . A factor that can occasionally cause a shift in the C–H stretching frequencies is ring strain. In particular, decreasing ring size raises the C–H frequency.<sup>11</sup> The band at 2800  $cm^{-1}$  may be thus ascribed to the presence in **2** of an eight-membered metallo ring, which can be accomplished only when the  $np_3$  nitrogen atom is not bonded to cobalt. Surely, the electronic configuration of the metal plays a very important role in determining whether the nitrogen atom of  $np_3$  is bound or not to the metal. Addition of a further ligand to the  $(np_3)M$  ( $M = Co, Ni$ ) moieties often would cause the formation of “supersaturated” species, which can be avoided by detaching one of the four donor atoms of  $np_3$  from the metal. The “decoordination” of the nitrogen atom has been so far reported for the complexes  $(np_3)Ni(CO)$ ,<sup>12</sup>  $(np_3)Ni(P_4)$ ,<sup>13</sup> and  $(np_3)Co(\eta^3-P_3)$ .<sup>14</sup> In the present com-

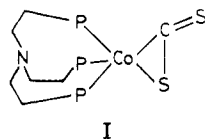
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plex 2, where the CS<sub>2</sub> molecule is assumed to donate two electrons to the d<sup>9</sup> cobalt atom, only three electron pairs from np<sub>3</sub> are required by the central atom to reach the 17-outer-electron configuration, which is particularly stable for cobalt.<sup>10</sup>

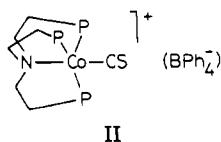
On the basis of all these data, it is therefore reasonable to formulate 2 as (np<sub>3</sub>)Co(η<sup>2</sup>-CS<sub>2</sub>) and to assign the structure I, where the cobalt atom is five-coordinate by three phosphorus atoms of np<sub>3</sub> and by a C=S linkage.



On concentration of the filtrate of the reaction mixture leading to 2 and addition of NaBPh<sub>4</sub> a few red crystals of empirical formula [(np<sub>3</sub>)Co(CS)]BPh<sub>4</sub> (3) can be isolated. Significant amounts of 3 can be synthesized by adding NaBPh<sub>4</sub> to a mixture of 1 and CS<sub>2</sub> in tetrahydrofuran.

3 is diamagnetic and air stable both in the solid state and in solution. It is soluble in common organic solvents, in which it behaves as a 1:1 electrolyte (molar conductance in 10<sup>-3</sup> M nitroethane solution is 42 cm<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup>). The electronic spectrum, practically unchanged both in the solid state and in solution, consists of a band at 22 000 cm<sup>-1</sup> (ε 3500) and is fully comparable with those of five-coordinate Co(I) complexes.<sup>9</sup> The IR spectrum exhibits a strong absorption at 1270 cm<sup>-1</sup>, which we assign to the ν(CS) stretching vibration of a terminal thiocarbonyl group.<sup>1a</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in CDCl<sub>3</sub> at -70 °C shows a singlet at 48.50 ppm. The large deshielding (coordination chemical shift of 68.06 ppm) found for this complex suggests that a ring contribution is present, indicating that no coordination change occurs on going from solid state to solution.<sup>15</sup>

A preliminary X-ray analysis<sup>16</sup> performed on 3 has shown that the cobalt atom is five-coordinate by the four donor atoms of np<sub>3</sub> and by a thiocarbonyl group (II). In particular, the bonding in the Co-C-S moiety is entirely analogous to that already well established for the Co-C-O grouping in the complex [(np<sub>3</sub>)Co(CO)]BPh<sub>4</sub> (4).<sup>17</sup>



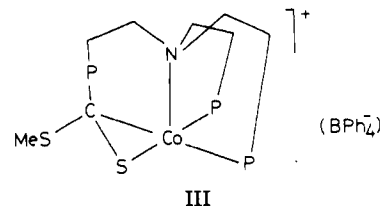
The magnetic and spectral data of 3 thus may be interpreted by means of the simple molecular orbital approach proposed for the carbonyl analogue 4,<sup>17</sup> by replacing the σ and π orbitals of CO with those of CS. The different energies of these CO and CS orbitals<sup>18</sup> (the 7σ donor orbital of CS is at higher energy than the 5σ orbital of CO, and the 3π(π\*) acceptor level of CS is at lower energy than the 2π(π\*) level of CO), in fact, should not afford dramatic changes in the molecular orbital diagram. The diamagnetism is thus in agreement with the (1e)<sup>4</sup>(2e)<sup>4</sup> configuration, and the band in the electronic spectrum at 22 200 cm<sup>-1</sup> is assigned to the <sup>1</sup>E[2e<sup>3</sup>2a<sub>1</sub>] ← <sup>1</sup>A<sub>1</sub>[2e<sup>4</sup>] transition.

Cobalt thiocarbonyls so far reported are extremely rare, being indeed limited to (C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)Co(CS) obtained by reaction of (C<sub>5</sub>H<sub>5</sub>)Co(PMe<sub>3</sub>)<sub>2</sub> with thiocarbonyl selenide.<sup>1e</sup>

At present no definitive conclusions are reached about the detailed mechanism for the formation of 3. In particular the fate of the sulfur has not been determined, but abstraction of np<sub>3</sub> to give (np<sub>3</sub>)S<sub>x</sub> (x = 1-3) apparently is not significant since no np<sub>3</sub> sulfides were detected. On the other hand, from the original mother liquor a brown powder containing cobalt, np<sub>3</sub>, and sulfur was isolated but not identified.

There is so far no general synthetic route to metal complexes containing terminal CS groups; however, η<sup>2</sup>-CS<sub>2</sub> complexes are often precursors to metal thiocarbonyls. The transformation of an η<sup>2</sup>-CS<sub>2</sub> molecule to a thiocarbonyl has been found to proceed through the following synthetic methods: (a) removal of one sulfur atom by a suitable sulfur acceptor as a tertiary phosphine;<sup>1a,18</sup> (b) alkylation of the exocyclic sulfur followed by alkanethiol elimination on subsequent reaction with acid or hydride ion;<sup>19</sup> (c) reaction with a further CS<sub>2</sub> molecule to form a head-to-tail bis(carbon disulfide) dimer that in turn can rearrange to give a CS ligand;<sup>20</sup> (d) reaction with an appropriate metal complex.<sup>21</sup> We succeeded in synthesizing the thiocarbonyl complex 3 from the η<sup>2</sup>-CS<sub>2</sub> complex 2 only through a procedure similar to method b, except for the alkylation product of the η<sup>2</sup>-CS<sub>2</sub> complex 2.

The reaction of a tetrahydrofuran suspension of 2 with MeSO<sub>3</sub>F, followed by addition of NaBPh<sub>4</sub> does not give the expected dithiomethyl ester complex, as in the case of the (triphos)Co(η<sup>2</sup>-CS<sub>2</sub>) complex.<sup>22</sup> Instead it affords brown crystals of the complex [Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Co(CS<sub>2</sub>Me)]BPh<sub>4</sub> (5) (III). The struc-



tural formulation given in III is not only based on the peculiar chemical and physical properties of 5, which are reported below, but is also mainly backed from the results of the complete X-ray analysis carried out on the isomorphous nickel derivative [Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Ni(CS<sub>2</sub>Me)]BPh<sub>4</sub>.<sup>23</sup> This compound can be prepared analogously to 5 by reaction of the η<sup>2</sup>-CS<sub>2</sub> complex (np<sub>3</sub>)Ni(η<sup>2</sup>-CS<sub>2</sub>) with MeSO<sub>3</sub>F.

Complex 5 is quite air stable in the solid state but decomposes in solution unless air is excluded. It is soluble in most organic solvents in which it behaves as a 1:1 electrolyte (molar conductance value in 10<sup>-3</sup> M nitroethane solution is 42 cm<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup>). The complex is paramagnetic with a room-temperature magnetic moment of 2.15 μ<sub>B</sub> corresponding to a doublet ground state and exhibits very similar solution (1,2-dichloroethane) and reflectance spectra which consist of absorptions at 5950 (ε 90), 7950 (60), 13 500 (130), 20 000 (790), and 22 500 cm<sup>-1</sup> (sh). The

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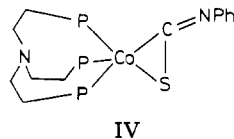
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pattern of these bands is in line with previously characterized five-coordinate low-spin Co(II) complexes.<sup>9</sup> The IR spectrum, practically superimposable to that of the nickel analogue, shows a band of medium intensity at 1100  $cm^{-1}$  attributable to a C=S stretching frequency. At variance with the parent complex 2, the band at 2800  $cm^{-1}$  is absent, thus indicating the coordination to the metal of the apical nitrogen atom of  $np_3$ .

A tetrahydrofuran suspension of complex 5 reacts with  $NaBH_4$ , giving the thiocarbonyl complex 3 and methanethiol. We have detected no intermediates nor have we made any kinetic measurements. Consequently many conceivable pathways can be proposed. However, the formation of complex 3 implies cleavages of MeS-C and P-CS<sub>2</sub>Me bonds. Cleavages of such bonds by the hydride ion from  $NaBH_4$  have indeed already reported. On reaction with  $NaBH_4$  the dithiomethyl ester complex cations  $[Os(\eta^2-CS_2Me)(CO)_2(PPh_3)_2]^+$  and  $[Ir(\eta^2-CS_2Me)Cl(CO)(PPh_3)_2]^+$  eliminate MeSH affording the thiocarbonyl complexes  $Os(CS)(CO)_2(PPh_3)_2$  and  $IrCl(CS)(PPh_3)_2$ ,<sup>19</sup> whereas the phosphonodithiocarboxylate complex  $[(dppe)_2Fe(S_2CPEt_3)](BPh_4)_2$  [dppe = 1,2-bis(diphenylphosphino)ethane] eliminates triethylphosphine, giving the dithioformate complex  $[(dppe)_2Fe(S_2CH)]BPh_4$ .<sup>24</sup>

The formation of the stable thiocarbonyl complex 3 by two different synthetic procedures confirms that the present scarcity of thiocarbonyl compounds is probably due to experimental procedure rather than the inherent instability of the complexes that are even more stable than the analogous carbonyl ones.<sup>1a,18</sup>

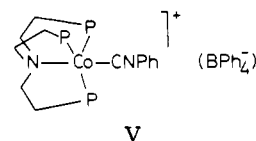
**Reaction with Phenyl Isothiocyanate.** A tetrahydrofuran suspension of 1 reacts with SCNPh producing a solution from which brick red crystals of  $(np_3)Co(\eta^2-SCNPh)$  (6) are obtained. Complex 6 is air stable in the solid state and fairly stable in solution in an inert atmosphere. The room-temperature  $\mu_{eff}$  is equal to 2.15  $\mu_B$ , corresponding to a doublet ground state. The reflectance spectrum with absorption maxima at 6750, 11 200, 19 600, and 21 700  $cm^{-1}$  is comparable with that of the  $\eta^2-CS_2$  complex 2. The IR spectrum shows bands at 1620 and 635  $cm^{-1}$  attributable to the C=N stretching vibration and the MSC vibration of a  $\eta^2-S,C$ -bonded SCNPh group.<sup>1b,7,25</sup> The band at 1620  $cm^{-1}$  is somewhat broadened by a phenyl vibration. Reinforced phenyl vibrations appear at 1575 and 1485  $cm^{-1}$ . The band at 2800  $cm^{-1}$  is also present, indicative of the decoordination of the nitrogen atom of  $np_3$ . A complete X-ray structural investigation has been carried out on 6.<sup>26</sup> The stereochemistry about the cobalt atom is essentially that found in  $(triphos)Ni(\eta^2-SCNPh)$ <sup>7</sup> and  $(triphos)Co(\eta^2-CS_2)$ ,<sup>10</sup> with the metal coordinated by the three phosphorus atoms of the  $np_3$  ligand and the C=S linkage of the heteroallene molecule (IV).



Since the synthesis of  $(PPh_3)_2Pt(\eta^2-SCNR)$  (R = Me, Ph) by Baird and Wilkinson in 1967,<sup>8</sup> few other  $\eta^2-C,S$ -bonded isothiocyanate complexes have been synthesized,<sup>1b,7,25,27</sup> and only one crystal structure, namely, that

of the complex  $(triphos)Ni(\eta^2-SCNPh)$ , has been so far reported.<sup>7</sup>

Although organo isothiocyanates react with many metal-ligand moieties, there are very few stable  $\eta^2-SCNR$  complexes. This has been ascribed to the great tendency of these molecules, when activated by metals, to undergo a variety of reactions such as the fragmentation to isocyanides,<sup>1e</sup> the condensation to bis SCNR dimers<sup>1e,28</sup> or dithiocarbimides,<sup>1e,29</sup> and the insertion into M-H bonds to give organo thioformamides.<sup>30</sup> The instability of  $\eta^2-SCNR$  may stem from the fact that there is a charge transfer from the metal to the heteroallene, with the consequent formation of reactive sites susceptible to attack by both nucleophilic and electrophilic agents. The observed stability of  $\eta^2-SCNPh$  complexes containing the tripodlike phosphines triphos and  $np_3$  may be connected with the presence of six phenyl rings that thus protect the heteroallene from facile attack by external reagents. Under suitable conditions, however, the  $\eta^2-SCNPh$  complex 6 can be converted into the isocyanide derivative  $[(np_3)Co(CNPh)]BPh_4$  (7) (V). Complex 7 is obtained as a red



solid by addition of  $NaBPh_4$  in ethanol to a methylene chloride solution of 6. It is air stable in the solid state and in solution, where it behaves as a 1:1 electrolyte (molar conductance in 10<sup>-3</sup> M nitroethane solution: 40  $cm^2 \Omega^{-1} mol^{-1}$ ). The spectral and magnetic properties of 7 are closely similar to those of the CS and CO analogues 3 and 4. The IR spectrum shows a band at 2060  $cm^{-1}$  assigned to the  $\nu(CN)$  vibration of the CNPh ligand.<sup>31</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of a singlet at 47.97 ppm.

The isolation of either the  $\eta^2-SCNPh$  complex 6 or the CNPh complex 7 helps to elucidate some reactions of metal complexes with organo isothiocyanates. In particular, those reactions leading to isocyanide<sup>1e</sup> or isocyanide-dithiocarbimido complexes,<sup>1e,29</sup> for which a mechanism involving an  $\eta^2$ -isothiocyanate complex as an intermediate has been postulated.

**Reaction with Phenyl Isocyanate.** A suspension of 1 in tetrahydrofuran reacts with OCNPh producing an intense red-orange solution. Fast evaporation of the major part of the solvent, followed by addition of *n*-pentane, precipitates orange crystals (8), which are quickly filtered. This paramagnetic compound is unstable even in the solid state so as to preclude a satisfactory characterization. However, we succeeded in recording its IR and electronic spectra. The IR spectrum is very similar to that of the  $\eta^2-SCNPh$  complex 6 showing bands at 2800, 1630, 1610, and 1345  $cm^{-1}$ . The reflectance spectrum exhibits absorption maxima at 8200, 16 100 (sh), and 22 000  $cm^{-1}$ .

On the basis of all these data it should be hazardous to assign a structure to 8. By analogy with complexes 2 and 6, a structure can be tentatively proposed where the  $np_3$  ligand acts as a triphosphine ligand and the OCNPh molecule is  $\pi$  bonded to the metal. At this moment it is impossible to discriminate between  $\eta^2-C,N$ - or  $\eta^2-C,O$ -bonding modes. The pattern of the IR bands of 8 is

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somewhat in line with the  $\eta^2$ -C,N-bonding mode,<sup>1b,32</sup> whereas the close similarity between IR spectra of 8 and 6 may indicate the  $\eta^2$ -C,O-bonding mode. Previous reports on OCNr reactions with metal complexes do not help us to assign a structure to 8: few complexes with  $\eta^2$ -C,N bonding to metals<sup>1b,5,32</sup> and no complex with an  $\eta^2$ -C,O-bonded organo isocyanate have been synthesized. Moreover, no crystal structure of any  $\pi$ -bonded isocyanate complex has been so far reported.

Current studies are underway to try to synthesize crystals suited for X-ray analysis. This could be accomplished by changing both the phosphine ligand (different phosphorus substituents, skeleton of the ligand) and the metal (for example, the complex  $(\text{np}_3)\text{Ni}^9$  is isoelectronic with 1 and can participate in similar reactions).

The low yield as well as the instability of 8 probably stem from the facile cleavage of C=Y bonds (Y = O, NR) of OCNr which can result in the formation of carbonyl and nitrene ligands.<sup>5,32c</sup> Indeed, CO formation during the reaction of OCNPh with 1 is observed, as evidenced by the isolation of the carbonyl complex 4 by NaBPh<sub>4</sub> addition to the reaction mixture leading to 8.

**Reaction with Carbonyl Sulfide.** A tetrahydrofuran suspension of 1 reacts with COS producing a red-brown solution. All attempts to try to isolate any stable compound from this reaction mixture met without success. By contrast, addition of NaBPh<sub>4</sub> in butanol results in the precipitation of the carbonyl complex 4.

This result is not unexpected since carbonylation and abstraction of sulfur are more common reactions of COS than its coordination to metals in the intact form.<sup>8,1e,f</sup> The fragmentation of COS to give CO can proceed through several pathways.<sup>1f</sup> In the present case the formation of a labile  $\eta^2$ -COS complex appears to be favored since the capability of the  $(\text{np}_3)\text{Co}$  moiety to give  $\eta^2$ -heteroallene complexes is well established. Moreover, this mechanism has been already suggested for example in the reaction of

the complex  $(\text{C}_5\text{H}_5)\text{Co}(\text{PMe}_3)_2$  with COS leading to  $(\text{C}_5\text{H}_5)\text{Co}(\text{PMe}_3)(\text{CO})$ ,<sup>1e</sup> isoelectronic with 4.

### Conclusions

Transition-metal fragments formed by tripod-like ligands such as  $\text{np}_3$  or triphos are well suited for the activation of the heteroallenes of formula  $\text{X}=\text{C}=\text{Y}$  (X, Y = O, S, NR, CR<sub>2</sub>). In particular these fragments not only coordinate these molecules<sup>6,7,10,23,33</sup> but also the products of their fragmentation<sup>33,34</sup> and insertion.<sup>35</sup> It is likely that the typical condensation reactions of heteroallenes which need vacant coordination sites on the metal are hindered by tripodlike ligands. On the other hand, these ligands may achieve coordination to the metal by using not all of their donor atoms, thus making the uncoordinated lone pairs available for eventual nucleophilic attack over unsaturated groups.<sup>23</sup>

Current studies are underway to investigate the reactivity of 1 as well as of other  $\text{np}_3$  and triphos metal complexes toward carbon dioxide. The observed decreasing stability on going from  $(\text{np}_3)\text{Co}(\eta^2\text{-CS}_2)$  to  $(\text{np}_3)\text{Co}(\eta^2\text{-COS})$  ( $\eta^2\text{-CS}_2 > \eta^2\text{-SCNPh} > \eta^2\text{-OCNPh} > \eta^2\text{-COS}$ ) makes the possible formation of an  $\eta^2\text{-CO}_2$  complex at least questionable. On the other hand, we are still confident that these tripodlike phosphine-metal fragments may act upon CO<sub>2</sub> since they can easily link groups such as CO, CO<sub>3</sub><sup>2-</sup>, and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> which are the common products of metal-CO<sub>2</sub> activation.<sup>1c</sup>

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**Registry No.** 1, 53687-39-1; 2, 87306-30-7; 3, 87306-32-9; 4, 54353-74-1; 5, 87306-34-1; 6, 87306-35-2; 7, 87306-37-4; 8, 87306-38-5; CS<sub>2</sub>, 75-15-0; SCNPh, 103-72-0; OCNPh, 103-71-9; COS, 463-58-1.

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