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# ALTERNATIVE ROUTES TO THE SYNTHESIS OF THE COBALT THIOCARBONYL COMPLEX $[(np_3)Co(CS)]BPh_4$. INFLUENCE OF THE Co–H DISSOCIATION PATHWAY ON THE REACTION OF THE HYDRIDE $(np_3)CoH$ WITH HETEROCUMULENES ($np_3$ = tris(2-diphenylphosphinoethyl)-amine)

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## Summary

Three routes to the synthesis of the cobalt(I) thiocarbonyl$[(np_3)Co(CS)]BPh_4$ (I) [$np_3$ = tris(2-diphenylphosphinoethyl)amine] are described, and their mechanisms briefly discussed. The structure of I has been determined from counter diffraction X-ray data. Crystal data are: $a$ 18.749(5), $b$ 34.494(10), $c$ 18.229(4) Å, $\beta$ 90.73(2)°, monoclinic space group $P2_1/a$, $Z = 8$. The structure has been solved by direct methods and refined to an $R$ of 0.097 using 1914 reflections with $I > 3.5\sigma(I)$. There are two independent molecules of the complex. The $[(np_3)Co(CS)]^+$ cations of the two molecules exhibit trigonal bipyramidal geometry around the cobalt atoms with the Co–CS fragments in a linear arrangement.

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Carbon monosulfide is an extremely unstable species which can be stabilized by coordination to a metal center. The preparation of metal thiocarbonyl complexes thus requires indirect synthetic routes. The currently available procedures exploit the reaction of suitable metal complexes with molecules containing a C=S grouping, such as $CS_2$, CSSe, $Cl_2CS$, or ClC(S)OR (R = Me, Et) [1,2] but it is difficult to predict the reaction path which some of these species will follow. Thus a general strategy for the preparation of thiocarbonyl complexes is not yet available, but despite this difficulty, well over 100 thiocarbonyl complexes have been reported. Many of these obtained were not completely characterized, however, and X-ray diffraction studies have been limited to less than 20 such complexes, including those with terminal and bridging CS ligands.

In an earlier paper we reported the preparation and the physical and chemical properties of the cobalt(I) thiocarbonyl complex $[(np_3)Co(CS)]BPh_4$ (I) [$np_3$ = tris(2-diphenylphosphinoethyl)amine] [3]. We now present further details of the synthesis

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of I and describe a new route to thiocarbonyl complexes. The structure of I has been elucidated by means of a complete X-ray diffraction analysis. This is of particular interest since only one cobalt thiocarbonyl was previously known, namely $(C_5H_5)(PMe_3)Co(CS)$, which was characterized by spectroscopic methods [4].

## Experimental

All the chemicals and solvents employed were of reagent-grade and were used without further purification. All the reactions described were performed under dry nitrogen unless otherwise stated. The solid complexes were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether (b.p. 40–70 °C) before being dried in a stream of dry nitrogen. Infrared spectra were recorded on a Perkin–Elmer 283 spectrophotometer as Nujol mulls between KBr plates. Proton and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian CFT 20 spectrometer. Peak positions are relative to tetramethylsilane and phosphoric acid, respectively, with downfield shifts positive. 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 with a WTW model LBR/B conductivity bridge.

*$[(np_3)Co(CS)]BPh_4$ (I).* A solution of $(np_3)Co(SCNPh)$ (VI) [3] (0.42 g, 0.5 mmol) in $CH_2Cl_2$ (30 ml) was treated with neat $MeOSO_2CF_3$ (0.066 ml, 0.6 mmol). There was an immediate color change from red orange to greenish red and within 1 h the solution turned dark red. On addition of $NaBPh_4$ (0.21 g, 0.6 mmol) in n-butanol (20 ml) and partial evaporation red orange crystals separated; yield 45%. Anal. Found: C, 74.71; H, 5.83; Co, 5.39; N, 1.22; S, 3.01. $C_{67}H_{62}BCoNP_3S$ calcd.: C, 74.79; H, 5.80; Co, 5.47; N, 1.30; S, 2.97%.

*$[(np_3)Co(O_2CNPhMe)](BPh_4)_2$ (VII).* The greenish red solution obtained by adding neat $MeOSO_2CF_3$ (0.066 ml, 0.6 mmol) to VI (0.42 g, 0.5 mmol) in $CH_2Cl_2$ (30 ml) was stirred in the air for 30 min, during which it turned to bright green. Addition of $NaBPh_4$ (0.42 g, 1.2 mmol) in ethanol (20 ml) led to the precipitation of green crystals; yield 50%. Anal. Found: C, 78.17; H, 6.14; Co, 4.00; N, 1.95; O, 2.10. $C_{98}H_{90}B_2CoN_2O_2P_3$ calcd.: C, 78.40; H, 6.04; Co, 3.92; N, 1.86; O, 2.13%.

### *X-ray data collection*

A red orange crystal of $[(np_3)Co(CS)]BPh_4$ chosen for the subsequent data collection was an elongated hexagonal prism with the following distances between the boundary faces: $(001)(00\bar{1})$, 0.475; $(010)(0\bar{1}0)$, 0.100; $(110)(\bar{1}\bar{1}0)$, 0.225; $(1\bar{1}0)(\bar{1}10)$, 0.250 mm. All X-ray measurements were carried out on a PW 1100 Philips diffractometer using Mo-$K_\alpha$ radiation (λ 0.71069 Å). The observed extinctions $(h0l)$ $h = 2n + 1$ and $(0k0)$ $k = 2n + 1$ indicated uniquely the monoclinic space group $P2_1/a$. The cell constants and orientation matrix were determined by least-squares refinement of the setting angle for 23 reflections. The crystal data are summarized in Table 1. The $\omega$–$2\vartheta$ scan technique was used to collect 5145 reflections up to $2\vartheta$ 44° with a scan speed of $0.07°\ s^{-1}$ and a scan width defined by equation $0.90 + 0.30\ tg\omega$. Three standard reflections were measured every 120 min but no decay was observed. The intensity data were corrected for Lorentz and polarization effects. Numerical absorption corrections have also been applied with the transmission factors ranging from 0.955 to 0.854. Of the reflections collected, 1914 had $I > 3.5\sigma(I)$, and these were used in the subsequent calculations. Atomic scattering factors were those given by Cromer and Waber [5], and anomalous dispersion corrections were taken from ref. 6.

*Solution and refinement of the structure*

The structure of the compound was solved by direct methods (MULTAN 80). An $F$ map based on 298 reflections with $|E| \geqslant 1.84$ indicated an existence of two independent complex molecules and revealed the locations of the cobalt, phosphorus, and nitrogen atoms as well as of some of the carbon atoms of the chains. The remaining non-hydrogen atoms were found from the subsequent Fourier maps computed using the SHELX 76 package [7]. The refinement of the structure faced several problems, since the number of parameters for 148 non-hydrogen atoms in the asymmetric unit was too large in comparison with the available data. To reduce the problems the phenyl rings were refined as rigid bodies of the $D_{6h}$ symmetry with all the carbon atoms having the same temperature factors. High thermal parameters, especially for atoms from the complex cation of the molecule 1, suggested a significant degree of disorder, although difference maps, while showing very diffuse electron density in the regions of interest did not allow recognition of the alternative occupation sites. In contrast, the atoms of the $BPh_4^-$ anions exhibited fairly typical thermal vibrations. Consequently, the contribution of the hydrogens from the tetraphenylborate phenyl rings in their idealized positions (C–H, 1.08 Å) were included in the calculations. All hydrogen atoms belonging to a particular ring were given the same temperature factors. A similar procedure was applied to the hydrogen atoms of the ethylenic chains, but in this case all the temperature factors were assumed to have the same value. The thermal parameters defined as above were subject to refinement. For the reasons described above no further hydrogen atoms were considered during calculations. The full-matrix least-squares refinement with anisotropic temperature factors for the cobalt and phosphorus atoms gave a final $R$ of 0.097 ($R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2 = 0.105$). The number of refined parameters was 302. The function minimized was defined as $\Sigma w(|F_o| - |F_c|)^2$ with the weights $w^{-1} = [\sigma^2(F) + 0.008\ F^2]$. As mentioned earlier, the final difference map showed several peaks of the height 0.3–0.45 e/Å$^3$ located in vicinity of the phenyl rings, the highest ones being near the ring R6. The final atomic coordinates for both independent molecules 1 and 2 are listed in Table 2, and values of selected

*(Continued on p. 96)*

TABLE 1

CRYSTAL DATA FOR $[(np_3)Co(CS)]BPh_4$

| | |
|---|---|
| Mol.formula | $C_{67}H_{62}BCoNP_3S$ |
| Mol.Wt | 1075.98 |
| $a$ (Å) | 18.749(5) |
| $b$ (Å) | 34.494(10) |
| $c$ (Å) | 18.229(4) |
| $\beta$(deg) | 90.73(2) |
| $V$ (Å$^3$) | 11788.2 |
| Space group | $P2_1/a$ |
| $Z$ | 8 |
| $d_{calcd}$ (g cm$^{-3}$) | 1.212 |
| $\mu$(Mo-$K_\alpha$) (cm$^{-1}$) | 4.42 |

TABLE 2

ATOMIC POSITIONAL PARAMETERS FOR [(np$_3$)Co(CS)]BPh$_4$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Co(1) | 7783(3) | 1342(2) | 5473(4) |
| Co(2) | 2484(3) | 1235(2) | 224(3) |
| P(1) | 7949(8) | 1493(4) | 6622(8) |
| P(2) | 8594(7) | 981(5) | 4911(8) |
| P(3) | 6774(7) | 1442(4) | 4928(9) |
| P(4) | 3256(7) | 1455(4) | −591(7) |
| P(5) | 2463(6) | 1493(4) | 1329(6) |
| P(6) | 1935(7) | 699(4) | −87(7) |
| N(1) | 7404(22) | 828(12) | 5845(21) |
| N(2) | 3266(19) | 879(11) | 596(19) |
| C(11) | 8130(26) | 1699(17) | 5172(27) |
| S(1) | 8462(13) | 2114(8) | 4865(13) |
| C(21) | 1879(25) | 1481(13) | −54(23) |
| S(2) | 1125(8) | 1756(5) | −296(8) |
| C(1) | 7584(27) | 1073(14) | 7105(26) |
| C(2) | 7161(26) | 821(15) | 6597(23) |
| C(3) | 8358(29) | 496(16) | 5140(28) |
| C(4) | 7859(27) | 487(14) | 5781(28) |
| C(5) | 6736(26) | 760(16) | 5434(28) |
| C(6) | 6210(37) | 974(20) | 4939(39) |
| C(7) | 4055(22) | 1272(12) | −235(23) |
| C(8) | 3934(22) | 900(12) | 180(22) |
| C(9) | 2961(21) | 1144(12) | 1837(23) |
| C(10) | 3545(22) | 994(14) | 1333(21) |
| C(12) | 2663(24) | 330(14) | 18(25) |
| C(13) | 3065(28) | 463(13) | 703(27) |
| C(1 1) | 8842(24) | 1561(11) | 7059(28) |
| C(2 1) | 8960(24) | 1515(11) | 7811(28) |
| C(3 1) | 9645(24) | 1563(11) | 8107(28) |
| C(4 1) | 10211(24) | 1657(11) | 7650(28) |
| C(5 1) | 10092(24) | 1702(11) | 6898(28) |
| C(6 1) | 9408(24) | 1655(11) | 6602(28) |
| C(1 2) | 7500(16) | 1922(17) | 7041(19) |
| C(2 2) | 7773(16) | 2285(17) | 6862(19) |
| C(3 2) | 7426(16) | 2620(17) | 7094(19) |
| C(4 2) | 6806(16) | 2592(17) | 7505(19) |
| C(5 2) | 6533(16) | 2228(17) | 7685(19) |
| C(6 2) | 6881(16) | 1893(17) | 7453(19) |
| C(1 3) | 9530(38) | 1006(15) | 5122(22) |
| C(2 3) | 9905(38) | 1292(15) | 4749(22) |
| C(3 3) | 10629(38) | 1350(15) | 4901(22) |
| C(4 3) | 10976(38) | 1121(15) | 5426(22) |
| C(5 3) | 10600(38) | 835(15) | 5799(22) |
| C(6 3) | 9877(38) | 777(15) | 5647(22) |
| C(1 4) | 8637(20) | 956(13) | 3922(29) |
| C(2 4) | 8921(20) | 624(13) | 3601(29) |
| C(3 4) | 8931(20) | 589(13) | 2838(29) |
| C(4 4) | 8657(20) | 885(13) | 2398(29) |
| C(5 4) | 8373(20) | 1217(13) | 2720(29) |
| C(6 4) | 8363(20) | 1252(13) | 3482(29) |
| C(1 5) | 6722(18) | 1576(9) | 3953(34) |
| C(2 5) | 6598(18) | 1320(9) | 3372(34) |
| C(3 5) | 6613(18) | 1454(9) | 2651(34) |

TABLE 2 (continued)

| Atom | x | y | z |
|---|---|---|---|
| C(4 5) | 6751(18) | 1845(9) | 2509(34) |
| C(5 5) | 6875(18) | 2101(9) | 3090(34) |
| C(6 5) | 6860(18) | 1967(9) | 3811(34) |
| C(1 6) | 6147(14) | 1795(13) | 5300(18) |
| C(2 6) | 6426(14) | 2137(13) | 5596(18) |
| C(3 6) | 5969(14) | 2429(13) | 5831(18) |
| C(4 6) | 5232(14) | 2380(13) | 5770(18) |
| C(5 6) | 4953(14) | 2039(13) | 5474(18) |
| C(6 6) | 5410(14) | 1746(13) | 5239(18) |
| C(1 7) | 3440(22) | 1996(21) | −702(22) |
| C(2 7) | 2876(22) | 2249(21) | −857(22) |
| C(3 7) | 2993(22) | 2648(21) | −869(22) |
| C(4 7) | 3674(22) | 2795(21) | −725(22) |
| C(5 7) | 4238(22) | 2543(21) | −570(22) |
| C(6 7) | 4121(22) | 2144(21) | −558(22) |
| C(1 8) | 3132(15) | 1275(10) | −1522(23) |
| C(2 8) | 3644(15) | 1070(10) | −1913(23) |
| C(3 8) | 3506(15) | 961(10) | −2638(23) |
| C(4 8) | 2856(15) | 1057(10) | −2972(23) |
| C(5 8) | 2344(15) | 1262(10) | −2581(23) |
| C(6 8) | 2482(15) | 1371(10) | −1855(23) |
| C(1 9) | 2912(21) | 1948(21) | 1540(23) |
| C(2 9) | 2804(21) | 2222(21) | 987(23) |
| C(3 9) | 3095(21) | 2592(21) | 1058(23) |
| C(4 9) | 3495(21) | 2689(21) | 1682(23) |
| C(5 9) | 3602(21) | 2415(21) | 2236(23) |
| C(6 9) | 3312(21) | 2045(21) | 2165(23) |
| C(110) | 1649(18) | 1556(8) | 1848(18) |
| C(210) | 1385(18) | 1250(8) | 2264(18) |
| C(310) | 750(18) | 1294(8) | 2646(18) |
| C(410) | 379(18) | 1644(8) | 2612(18) |
| C(510) | 643(18) | 1951(8) | 2196(18) |
| C(610) | 1278(18) | 1907(8) | 1813(18) |
| C(111) | 1185(23) | 521(8) | 454(20) |
| C(211) | 760(23) | 789(8) | 821(20) |
| C(311) | 168(23) | 663(8) | 1210(20) |
| C(411) | 1(23) | 269(8) | 1233(20) |
| C(511) | 425(23) | 1(8) | 865(20) |
| C(611) | 1017(23) | 127(8) | 476(20) |
| C(112) | 1587(22) | 609(9) | −1029(21) |
| C(212) | 913(22) | 756(9) | −1205(21) |
| C(312) | 620(22) | 694(9) | −1902(21) |
| C(412) | 1000(22) | 486(9) | −2424(21) |
| C(512) | 1675(22) | 340(9) | −2248(21) |
| C(612) | 1968(22) | 401(9) | −1551(21) |
| B(1) | 3093(28) | 754(16) | 4168(29) |
| C(113) | 2418(17) | 516(7) | 3654(12) |
| C(213) | 1734(17) | 550(7) | 3940(12) |
| C(313) | 1155(17) | 382(7) | 3572(12) |
| C(413) | 1259(17) | 181(7) | 2919(12) |
| C(513) | 1943(17) | 147(7) | 2633(12) |
| C(613) | 2522(17) | 315(7) | 3001(12) |
| C(114) | 2852(17) | 1163(11) | 4407(14) |
| C(214) | 2424(17) | 1391(11) | 3948(14) |

TABLE 2 (continued)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(314) | 2230(17) | 1764(11) | 4166(14) |
| C(414) | 2464(17) | 1908(11) | 4842(14) |
| C(514) | 2892(17) | 1680(11) | 5300(14) |
| C(614) | 3086(17) | 1307(11) | 5083(14) |
| C(115) | 3869(15) | 775(7) | 3614(15) |
| C(215) | 4160(15) | 434(7) | 3340(15) |
| C(315) | 4738(15) | 449(7) | 2867(15) |
| C(415) | 5024(15) | 806(7) | 2667(15) |
| C(515) | 4733(15) | 1148(7) | 2940(15) |
| C(615) | 4155(15) | 1133(7) | 3414(15) |
| C(116) | 3325(16) | 459(8) | 4881(16) |
| C(216) | 4034(16) | 368(8) | 5051(16) |
| C(316) | 4197(16) | 152(8) | 5678(16) |
| C(416) | 3653(16) | 28(8) | 6136(16) |
| C(516) | 2945(16) | 119(8) | 5967(16) |
| C(616) | 2781(16) | 334(8) | 5339(16) |
| B(2) | 1591(32) | 3995(18) | −64(33) |
| C(117) | 1374(17) | 4354(10) | 523(14) |
| C(217) | 767(17) | 4582(10) | 422(14) |
| C(317) | 608(17) | 4872(10) | 928(14) |
| C(417) | 1055(17) | 4933(10) | 1535(14) |
| C(517) | 1662(17) | 4704(10) | 1635(14) |
| C(617) | 1822(17) | 4415(10) | 1129(14) |
| C(118) | 2466(22) | 3928(10) | −91(18) |
| C(218) | 2839(22) | 3718(10) | 443(18) |
| C(318) | 3581(22) | 3694(10) | 419(18) |
| C(418) | 3950(22) | 3879(10) | −141(18) |
| C(518) | 3577(22) | 4089(10) | −675(18) |
| C(618) | 2835(22) | 4114(10) | −650(18) |
| C(119) | 1222(17) | 4103(8) | −880(19) |
| C(219) | 844(17) | 3817(8) | −1260(19) |
| C(319) | 553(17) | 3896(8) | −1952(19) |
| C(419) | 641(17) | 4262(8) | −2264(19) |
| C(519) | 1019(17) | 4548(8) | −1884(19) |
| C(619) | 1310(17) | 4469(8) | −1192(19) |
| C(120) | 1199(17) | 3588(8) | 265(17) |
| C(220) | 695(17) | 3591(8) | 821(17) |
| C(320) | 411(17) | 3243(8) | 1075(17) |
| C(420) | 633(17) | 2892(8) | 775(17) |
| C(520) | 1138(17) | 2889(8) | 219(17) |
| C(620) | 1421(17) | 3237(8) | −36(17) |

parameters in Table 3. Tables of thermal parameters and structure factors are available from the authors.

## Results and discussion

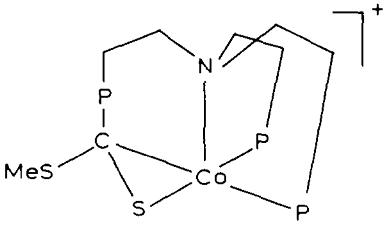
The complex $[(np_3)Co(CS)]BPh_4$ (I) can be synthesized by the two routes 1 and 2 [3]. A THF suspension of the phosphoniodithiomethylester complex

$[Ph_2\overline{PCH_2CH_2N(CH_2CH_2PPh_2)_2Co(C}S_2Me)]BPh_4$ (II) reacts with $NaBH_4$ to give

$$\left[Ph_2\overline{PCH_2CH_2N(CH_2CH_2PPh_2)_2Co\big(C}S_2Me\big)\right]BPh_4 + NaBH_4 \rightarrow$$
$$[(np_3)Co(CS)]BPh_4 + MeSH \qquad (1)$$

$$(np_3)CoH + CS_2 + NaBPh_4 \rightarrow [(np_3)Co(CS)]BPh_4 \qquad (2)$$

I and methylthiol. The formation of the thiocarbonyl complex clearly implies the cleavage of both the MeS–CS and P–$CS_2$Me bonds. Such cleavages are not altogether surprising, since both phosphoniodithiocarboxylate [8] and dithiomethyl ester ligands [9] have been found to react with $NaBH_4$ to give dithioformato or thiocarbonyl complexes, respectively. However the unusual nature of the phosphoniodithiomethyl ester complex II prevents direct comparison with any other reaction reported in the literature; and any attempt to rationalize the reaction is complicated by the unusual flexibility shown by $np_3$. This ligand, which normally acts as a tetradentate species giving rise to $C_{3v}$ metal fragments of the $L_4M$ type [10] (this is the coordination in the thiocarbonyl complex I), is tridentate in both the precursor complex $(np_3)Co(\eta^2\text{-}CS_2)$ (III) [3] and the methylated derivative II [3]. Even more puzzling is that in the latter cases two different bonding modes are found: whereas the apical nitrogen atom is not coordinated to the metal in III, in II the atom not coordinated is one of the phosphorus donors. However, a reasonable



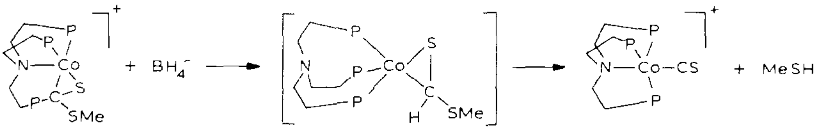
(II)

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) IN $[(np_3)Co(CS)]BPh_4$

| | | | |
|---|---|---|---|
| Co(1)–P(1) | 2.18(2) | Co(2)–P(4) | 2.22(2) |
| Co(1)–P(2) | 2.23(2) | Co(2)–P(5) | 2.20(2) |
| Co(1)–P(3) | 2.15(2) | Co(2)–P(6) | 2.19(2) |
| Co(1)–N(1) | 2.03(6) | Co(2)–N(2) | 2.03(5) |
| Co(1)–C(11) | 1.50(8) | Co(2)–C(21) | 1.50(7) |
| S(1)–C(11) | 1.66(8) | S(2)–C(21) | 1.76(7) |
| P(1)–Co(1)–P(2) | 119.1(9) | P(4)–Co(2)–P(5) | 119.5(7) |
| P(1)–Co(1)–P(3) | 121.3(9) | P(4)–Co(2)–P(6) | 115.1(7) |
| P(2)–Co(1)–P(3) | 118.6(9) | P(5)–Co(2)–P(6) | 124.3(8) |
| P(1)–Co(1)–N(1) | 86(2) | P(4)–Co(2)–N(2) | 88(2) |
| P(2)–Co(1)–N(1) | 85(2) | P(5)–Co(2)–N(2) | 88(2) |
| P(3)–Co(1)–N(1) | 89(2) | P(6)–Co(2)–N(2) | 85(2) |
| P(1)–Co(1)–C(11) | 96(3) | P(4)–Co(2)–C(21) | 94(2) |
| P(2)–Co(1)–C(11) | 90(3) | P(5)–Co(2)–C(21) | 93(2) |
| P(3)–Co(1)–C(11) | 95(3) | P(6)–Co(2)–C(21) | 92(2) |

reaction pathway could involve an initial attack by an hydride ion from $NaBH_4$ on the carbon atom of the fragment $P\text{-}CS_2Me$, with subsequent formation of an unstable $\eta^2$-C,S bonded methyldithioformate ligand. The observed extrusion of MeSH from the latter complex could then lead to the thiocarbonyl complex I (eq. 3).



(3)

Alternatively, I can be synthesized by direct reaction of the complex $(np_3)CoH$ (IV) [10] with $CS_2$ in the presence of $NaBPh_4$. All our attemps to determine the fate of the other sulfur were unsuccessful. From the original mother liquor a brown powder containing cobalt, $np_3$, and sulfur was isolated, but it was not identified.

Understanding the nature of this reaction would be easier if the nature of the hydrogen in IV was established, and the following results provide valuable clues:
(a) Compound IV reacts with heteroallene molecules of formula X=C=Y (X, Y = O, S, NPh) to give the corresponding paramagnetic cobalt(0) $\eta^2$-complexes [3] (Scheme 1); in all of these compounds the nitrogen atom of $np_3$ is not coordinated to the metal center.
(b) When the same reactions are carried out in the presence of $NaBPh_4$, there is the

$$(np_3)CoH \xrightarrow{CS_2} (np_3)Co(\eta^2\text{-}CS_2)$$
$$(np_3)CoH \xrightarrow{SCNPh} (np_3)Co(\eta^2\text{-}SCNPh)$$
$$(np_3)CoH \xrightarrow{OCNPh} (np_3)Co(\eta^2\text{-}PhNCO)$$
$$(np_3)CoH \xrightarrow{CO_2} \text{no reaction}$$

SCHEME 1

fragmentation of the heteroallene molecules and the cobalt(I) complexes specified below are formed (Scheme 2) [3,11]; there is evidence that $np_3$ is tetradentate in all these compounds.

$$(np_3)CoH + NaBPh_4 \xrightarrow{CS_2} [(np_3)Co(CS)]BPh_4$$
$$(np_3)CoH + NaBPh_4 \xrightarrow{SCNPh} [(np_3)Co(CNPh)]BPh_4$$
$$(np_3)CoH + NaBPh_4 \xrightarrow{OCNPh} [(np_3)Co(CO)]BPh_4$$
$$(np_3)CoH + NaBPh_4 \xrightarrow{CO_2} [(np_3)Co(CO)]BPh_4$$

SCHEME 2

(c) Compound IV reacts with methylating agents or with $HBF_4$ according equations 4 and 5. The complexes $[(np_3)Co]Y$ ($Y = SO_3CF_3$, $BF_4$, $BPh_4$) (V) are paramagnetic

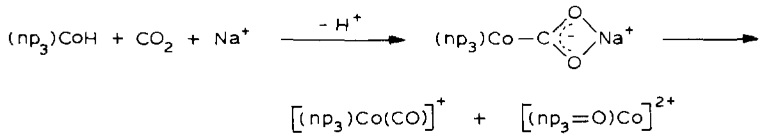
$$(np_3)CoH + MeOSO_2CF_3 \rightarrow [(np_3)Co]SO_3CF_3 + CH_4 \qquad (4)$$

$$(np_3)CoH + HBF_4 \rightarrow [(np_3)Co]BF_4 + H_2 \qquad (5)$$

with a $\mu_{eff}$ corresponding to three unpaired spin. The compound with a $BF_4^-$ counterion has been made previously from $Co(BF_4)_2 \cdot 6H_2O$, $np_3$ and an equimolecular amount of $NaBH_4$ [12]. An X-ray crystal structure determination showed that the cobalt(I) cation $[(np_3)Co]^+$ has a trigonal-pyramidal structure;

(d) Compounds V do not react with the heterocumulenes listed above.

In summary, there is ample evidence that the hydrogen atom leaves the $(np_3)CoH$ complex as an hydride during the reactions of type c, whereas the result described in (d) suggests that the cleavage of the cobalt–hydrogen bond might occur in a homolytic way. However, none of these mechanisms seems to favour the fragmentation reactions reported in Scheme 2. On the other hand, an equilibrium of the type $(np_3)CoH \rightleftharpoons (np_3)Co^- + H^+$ may perhaps operate in polar media. In this case the trigonal pyramidal $d^{10}$ metal fragment with a lone pair directed toward the unoccupied site of the bipyramid could favour a C-coordination of the X=C=Y molecules, which are electrophilic at the central carbon atom. The cleavage of either the C–X or C–Y bond may eventually follow. The reaction of IV with $CO_2$ in the presence of sodium ions has been suggested to proceed by pathway 4 [11]. The $np_3$=O complex ($np_3$=O = $O{=}PPh_2CH_2CH_2N(CH_2CH_2PPh_2)_2$) is probably formed through intermolecular attack by a phosphorus atom of coordinated $np_3$ on a $CO_2$ molecule activated by the interaction with the metal center.



(6)

Some metal hydride complexes are hydrogen atom donors in radical-chain processes. On the other hand, some complexes release hydridic hydrogen with ease, while some others behave as acids, either weak or strong [13]. $(CO)_4CoH$, for example is as strong as a mineral acid, but the acid strength falls when the CO groups are replaced by phosphine molecules [14]. In the light of the evidence presented above, the complex $(np_3)CoH$ can be regarded as unique, since it may release hydrogen atoms or $H^+$ or $H^-$ species, depending on the particular type of reaction involved. An important factor role in determining the behaviour of IV must be the unique bonding capabilities of the ligand $np_3$. In effect this may envelope the metal in different ways which ultimately affect the mobility of hydrogen over the coordination sphere and hence influence the mode of rupture of the M–H linkage.

Elian and Hoffmann [15] established the theoretical bases which determine the relationship between the geometry of the complex and the nature of the coordinated hydrogen atom. In particular, the latter is most hydridic if it occupies an apical position of a trigonal bipyramidal $d^8$ complex; the complex becomes a potential proton donor when the other four ligands are tetrahedrally arranged. Even in this case a negative charge on the hydrogen cannot be excluded, but the charge delocalization from the metal is significantly reduced and a weaker M–H bond easily broken in presence of polar solvents, ensues. Experimental evidence, relevant to these points has been recently reported for $(CO)_4CoH$ [14].

Due to the steric requirements of the $np_3$ ligand, IV adopts a trigonal bipyramidal coordination. The complex is isostructural with the isoelectronic cation $[(np_3)NiH]^+$ [16]. The $^1H$ NMR spectrum of IV in $C_6D_6$ at room temperature, showing a quadruplet at $\delta$ 25.93 ($J$(P–H) 50.9 Hz), is similar to that of $[(np_3)NiH]^+$ [17] ($CD_3COCD_3$, 293 K, quadruplet centered at $\delta$ 23.2 ppm, $J$(P–H) 37.5 Hz). The latter compound has been shown to undergo an intramolecular migration upon attack of a CO molecule to bring the hydrogen atom, as a proton, over the apical amine nitrogen of $np_3$. This nitrogen atom is no longer coordinated to the metal, which is now tetrahedral, since CO has entered the coordination sphere (Fig. 1) [16]. Similarly the addition of pyridine to a benzene solution of IV, removes the hydride resonance and a new broad singlet appears at $\delta$ 13.89 ppm. Resonances in this region are usually attributed to N–H protons [16,18]. However, this result must be interpreted with caution since some decomposition takes place as evidenced by the appearance of a flocculent precipitate. Furthermore, broad singlets in the same region appear if solutions of IV are left to stand for 1–2 h in the NMR tube.

To summarize, when the trigonal bipyramidal coordination replaced by a tetrahedral one (the process is made possible by a rearrangment of $np_3$ which removes the apical nitrogen from the metal and allows a new coligand to enter), the metal–hydride complex becomes a potential proton donor.

In conclusion, there is sufficient evidence that, depending on the reaction conditions, three different species, namely $(np_3)Co^+$, $(np_3)Co^-$, and $(np_3)Co$ , can be formed from the complex $(np_3)CoH$. Of these, only the last two only seem to be reactive toward heterocumulenes X=C=Y, each of them showing various reaction pathways.

A third route to the thiocarbonyl complex I is also available. A $CH_2Cl_2$ solution of the phenylisothiocyanate complex $(np_3)Co(\eta^2\text{-}SCNPh)$ (VI) [3] reacts with $MeOSO_2CF_3$ to give a dark red solution. Addition of $NaBPh_4$ gives red orange crystals of I in good yield. In an attempt to determine the fate of the NPh group in this reaction, we exposed the mixture of VI and $MeOSO_2CF_3$ to the air. In a few minutes the color of the solution changed to bright green. On addition of $NaBPh_4$ diamagnetic green crystals separated. This compound is air-stable in the solid state and in solution. It is fairly soluble in common organic solvents, in which it behaves as a 1/2 electrolyte (molar conductance in $10^{-3}$ $M$ nitroethane solution: 102 $cm^2$ $ohm^{-1}$ $mol^{-1}$). The reflectance spectrum consists of bands at 25000 and 16000 $cm^{-1}$, and is comparable with that of the six-coordinate cobalt(III) complex $[(np_3)CoCl_2]BF_4$ [19].

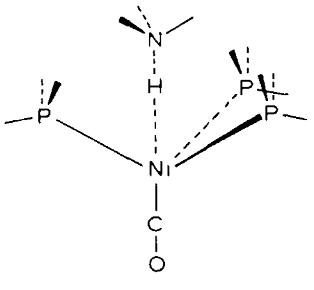
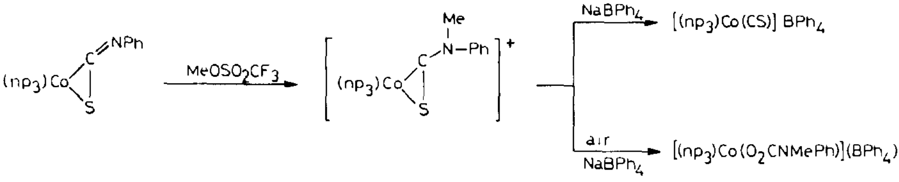


Fig. 1. Sketch drawing of the product of the reaction between $[(np_3)NiH]^+$ and CO.

The analytical and spectroscopic data for this complex suggest the presence of the carbamate ligand $MePhNCO_2^-$ in a complex which may be formulated as $[(np_3)Co(O_2CNPhMe)](BPh_4)_2$ (VII). The $^{31}P\{^1H\}$NMR spectrum in $CD_3COCD_3$ at −60°C shows a triplet at $\delta$ 32.87 ppm ($J$(P–P) 40 Hz) and a doublet at 18.00 ppm (intensity ratio 1/2). This pattern may be tentatively assigned to an octahedral geometry of the complex, bearing in mind that the $np_3$ ligand can adapt to such a coordination, as found for the complex cation $[(np_3)CoCl_2]^+$ [19]. The $^1H$ NMR spectrum in $CD_2Cl_2$ at room temperature exhibits a resonance at $\delta$ 3.13 ppm, characteristic of the $CH_3$ group of *N*-methyl carbamate complexes [20]. The IR spectrum shows a medium band at 1545 $cm^{-1}$, which is typical of the C–N stretch of carbamate ligands [20,21].

The formation of both the thiocarbonyl and the carbamate complex may be rationalized by assuming that there is preliminary formation of a thiocarboxamido ligand, which then undergoes fragmentation to carbon monosulfide and amido groups. The CS fragment can be stabilized by the metal, whereas the amido group can be trapped by reaction with $CO_2$ present in the atmosphere to give a carbamate ligand. In the latter case, the presence of oxygen seems to be essential for formation of compound VII. In addition other roles which so far are unknown, oxygen must certainly be responsible for increasing the oxidation number of cobalt to +3 (Scheme 3).



SCHEME 3

As regards the formation of the thiocarboxamido intermediate, alkylation of the nitrogen atom is a known, though rare, reaction path for dihapto-organoisothiocyanate metal complexes. For instance, the complex $Os(\eta^2\text{-}SCN\text{-}p\text{-}tolyl)(CS)(CO)(PPh_3)$ is methylated by MeI to form the dihapto-thiocarboxamido cation $[Os(\eta^2\text{-}SCNMe\text{-}p\text{-}tolyl)(CS)(CO)(PPh_3)]^+$ [22]. As in the case of $\eta^2$-$CS_2$ complexes, the dihapto-coordination localizes most of the charge donated by the metal on the uncoordinated atom of the heteroallene.

## Description of the structure

The structure of the compound consists of two independent formula units with separate $[(np_3)Co(CS)]^+$ cations and tetraphenylborate anions. The molecular structure of the $[(np_3)Co(CS)]^+$ moieties is depicted in Fig. 2. Both cations exhibit trigonal bipyramidal coordination around the cobalt atoms, with the $np_3$ tripod ligands chelated through the three phosphorus atoms and the nitrogen atoms bonded in the apical position. The thiocarbonyl groups located *trans* to the nitrogen atoms complete the coordination sphere. Because of the experimental difficulties mentioned previously the standard deviations are high, and the results obtained must be treated with caution. This is particularly the case for the thiocarbonyl groups, for which large thermal vibrations obscure more detailed analysis of the bonding system.

The situation is further complicated by the fact that, to our knowledge, this is the first X-ray structure determination performed for a terminal thiocarbonyl cobalt complex and consequently there are no data available for comparison of the Co–CS group geometry. On the other hand, other bond lengths and angles within the complex cations and the anions are normal. Thus, the Co–P distances, ranging from 2.15(2) to 2.23(2) Å, are close to those found in other Co-np$_3$ complexes [23], and the Co–N bond lengths also seem to have typical values 2.03(5) Å in both independent molecules. The Co–CS fragment is linear, the Co–C–S angles having values of 176(6)° (molecule 1) and 174(4)° (molecule 2). However, the Co–C distances (1.50(7) Å in both molecules) are much shorter than those observed in other transition metal complexes containing terminal thiocarbonyl groups [24–28]. They are also shorter than the Co–C bond length of 1.63(4) Å found in the carbonyl analogue of the complex described here [23]. Such shortening has been predicted by theoretical calculations, which indicate stronger $\sigma$-donor and $\pi$-acceptor abilities for the CS group compared with carbon monoxide [29,30]. The extent of the $\pi$ back-bonding from the metal $d\pi$ orbitals to the $\pi^*$ orbitals on the ligands increases in the series CNR < CO < CS. Consequently, the Co–C distances in the Co-np$_3$ complexes with CS and CO are shorter than that of 1.87(2) Å observed in pentakis(methylisonitrile) cobalt(I) perchlorate [31], a cobalt(I) complex exhibiting similar trigonal bypiramidal geometry. An excellent example of this effect is also provided by the X-ray structure of *trans*-$W(CO)_4(CNC_6H_{11})(CS)$ [32], which contains carbon monosulfide, carbon monoxide and cyclohexyl isocyanide ligands. Of the W–C bond distances, the W–CS value is the shortest (1.94(2) Å). The W–CO distances are longer, ranging from 2.05(2) to 2.09(2) Å, and the W–$CNC_6H_{11}$ distance is the longest, at 2.16(2) Å.

The C–S distances in the structure presented here are 1.66(8) and 1.76(7) Å (molecules 1 and 2, respectively), and are thus larger than those in metal-terminal CS complexes [24–28].

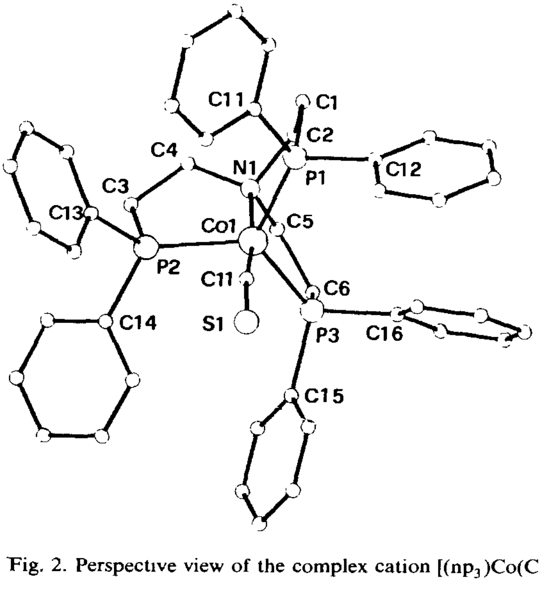


Fig. 2. Perspective view of the complex cation $[(np_3)Co(CS)]^+$ of the molecule 1.

## References

1 P.V. Yaneff, Coord. Chem. Rev., 23 (1977) 183.
2 I.S. Butler, Acc. Chem. Res., 16 (1977) 359.
3 C. Bianchini, A. Meli and G. Scapacci, Organometallics, 2 (1983) 1834.
4 H. Werner and O. Kolb, Angew. Chem. Int. Ed. Engl., 18 (1979) 865.
5 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974; Vol. 4, p. 99.
6 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974; Vol. 4, p. 149.
7 G.M. Sheldrick, SHELX-76, Program of Crystal Structure Determinations, University of Cambridge, Cambridge, 1976.
8 C. Bianchini, P. Innocenti, A. Meli, A. Orlandini and G. Scapacci, J. Organomet. Chem., 233 (1982) 233.
9 T.J. Collins, W.R. Roper and K.G. Town, J. Organomet. Chem., 121 (1976) C41.
10 L. Sacconi and F. Mani, Transition Metal Chem., 8 (1982) 179.
11 C. Bianchini and A. Meli, J. Am. Chem. Soc., 106 (1984) 2698.
12 L. Sacconi, A. Orlandini and S. Midollini, Inorg. Chem., 13 (1974) 2850.
13 J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, C.A., 1980.
14 R.L. Sweany and J.W. Owens, J. Organomet. Chem., 255 (1983) 327.
15 H. Elion and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
16 F. Cecconi, C.A. Ghilardi, P. Innocenti, C. Mealli, S. Midollini and A. Orlandini, Inorg. Chem., 23 (1984) 922.
17 S. Midollini, personal communication.
18 F. Calderazzo, G. Fachinetti, F. Marchetti and P.F. Zanazzi, J. Chem. Soc., Chem. Commun., (1981) 181.
19 M. Di Vaira, A. Meli and L. Sacconi, Cryst. Struct. Commun., 6 (1977) 727.
20 G. Chandra, A.D. Jenkins, M.F. Lappert and R.C. Srivastava, J. Chem. Soc. A, (1970) 2550.
21 F. Calderazzo, G. Dell'Amico, R. Netti and M. Pasquali, Inorg. Chem., 17 (1978) 472.
22 G.R. Clark, T.J. Collins, D. Hall, S.M. Jones and W.R. Roper, J. Organomet. Chem., 141 (1977) C5.
23 C.A. Ghilardi, A. Sabatini and L. Sacconi, Inorg. Chem., 15 (1976) 2763.
24 J.L. De Boer, D. Rogers, A.C. Skapski and P.G.H. Troughton, J. Chem. Soc., Chem. Commun., (1966) 756.
25 J.S. Field and P.J. Wheatley, J. Chem. Soc., Dalton Trans., (1972) 2269.
26 J.Y. Saillard, G. Le Borgne and D. Grandjean, J. Organomet. Chem., 94 (1975) 409.
27 J.D. Korp and I. Bernal, Cryst. Struct. Commun., 9 (1980) 821.
28 R. Usón, L.A. Oro, M.A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio Camellini, J. Organomet. Chem., 224 (1982) 69.
29 W.G. Richards, Trans. Faraday Soc., 63 (1967) 257.
30 D.L. Lichtenberger and R.F. Fenske, Inorg. Chem., 15 (1976) 2015.
31 F.A. Cotton, T.G. Dunne and J.S. Wood, Inorg. Chem., 4 (1965) 318.
32 S.S. Woodard, R.A. Jacobson and R.J. Angelici, J. Organomet. Chem., 117 (1976) C75.