Organometallics 1983, 2, 874-878

Substitution Reactions of Di-*tert*-butylphosphido Complexes of Nickel(I). Crystal Structures of $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_2(PMe_3)$ (Ni–Ni) and $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$ (Ni–Ni)

Richard A. Jones* and Anthony L. Stuart

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Jerry L. Atwood* and William E. Hunter

Department of Chemistry, The University of Alabama, University, Alabama 35486

Received November 2, 1982

Reaction of the dinuclear nickel(I) phosphide $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (1) with excess PEt_3 or $P(OMe)_3$ (L) in benzene yields $[Ni(\mu\text{-}t\text{-}Bu_2P)(L)]_2$ (2, L = PEt_3, or 3, L = $P(OMe)_3$) in high yield. The reaction of 1 or 2 with CO (1 atm) yields $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_2(PMe_3)$ (4) or $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_2(PEt_3)$ (5) in which only one phosphine group from one nickel atom has been replaced by two CO groups. 4 does not react with excess PMe_3 although with PEt_3 5 is formed in high yield. Reaction of 1 with $Mn_2(CO)_{10}$ in THF with UV irradiation yields $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$ (6) in ca. 50% yield. Interaction of 6 with PMe_3 gives 4 in high yield. The structure of 6 is similar to that of 4 with the PMe_3 group of 4 now replaced by CO. The structures of 4 and 6 have been determined by X-ray diffraction. Crystal data for 4: monoclinic, space group $P2_1/n$; $a = 8.673$ (4) Å, $b = 18.589$ (8) Å, $c = 17.828$ (8) Å, $\beta = 96.45$ (2)°, $U = 2856.2$ (5) Å^3, $D_{calcd} = 1.26$ g cm^{-3}, $Z = 4$ (dimers), $F(000) = 1152$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 14.93$ cm^{-1}, final $R = 0.049$, $R_w = 0.055$ from 1656 observed reflections (2171 measured). Crystal data for 6: monoclinic, space group $P2_1/n$; $a = 12.551$ (5) Å, $b = 13.209$ (6) Å, $c = 16.016$ (7) Å, $\beta = 108.98$ (3)°, $U = 2510.9$ (5) Å^3, $D_{calcd} = 1.30$ g/cm^{-3}, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 16.35$ cm^{-1}, final $R = 0.048$, $R_w = 0.057$ from 1610 observed (2488 measured) reflections.

Introduction

Several well-characterized phosphido or phosphinidene complexes of nickel are known although little has been reported of their chemistry.[1,2] For nickel(I), $[(CO)_2Ni(\mu\text{-}PPh_2)]_2$ and $Ni_2(\mu\text{-}PPh_2)_2(PEt_3)_3$[3] have been reported and recently complexes of the type $[(PR_3)Ni(\mu\text{-}(SiMe_3)_2P)]_2$[4] and also with μ-P(c-Hx)$_2$[5] (c-Hx = cyclohexyl) bridges were described. The poorly characterized nitrosyl $[Ni(NO)(PPh_2)]_4$ which is thought to be a tetramer has also been reported.[6] For nickel(II) well-characterized compounds include $[CpNi(\mu\text{-}PPh_2)]_2$,[7,8] $[CpNi(\mu\text{-}PMe_2)]_2$,[9] and $[CpNi(\mu\text{-}P(CF_3)_2]_2$.[10] There are also some poorly characterized complexes such as $[(Ph_2P)_2Ni]_n$ where $n = 5$ or 6[11] and $n = 2$[12] and several salts such as $Li[Ni(P(C_6H_{11})_2)_3]$[12] and $[(Ph_2P)_2Ni(CO)_2]K_2\cdot 2THF$.[13] Lastly Dahl has reported the synthesis and structure of the unusual Ni_8 cubic cluster $Ni_8(CO)_8(\mu_4\text{-}PPh)_6$.[14]

We recently reported the initial results of our preliminary investigation into the steric effects of phosphido (R_2P^-) ligands in organometallic chemistry.[15,16] Using di-*tert*-butyl phosphide ($t\text{-}Bu_2P^-$), we have been able to isolate and characterize a number of dinuclear and multinuclear complexes. We report here details of the chemistry of the nickel(I) dimer $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (1). The trimethylphosphine groups of 1 are readily replaced by other small phosphorus donors such as PEt_3 or $P(OMe)_3$ to give complexes of formula $[Ni(\mu\text{-}t\text{-}Bu_2P)(PR_3)]_2$ (2 or 3, respectively) which are isostructural with 1 on the basis of NMR data. However, interaction of 1 or 2 with CO yields the unusual asymmetric complexes $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_2L$ (L = PMe_3 (4), PEt_3 (5)) in which only one phosphine is replaced. 4 and 5 are inert to further substitution by CO, although 5 can be obtained from 4 by treatment with excess PEt_3. The asymmetric substitution pattern appears to be a feature of the system since reaction of 1 and $Mn_2(CO)_{10}$ with photolysis yields $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$ (6) which has a structure similar to 4 but with the PMe_3 group now replaced by one CO. 6 reacts with PMe_3 to give 4 but does not react further with CO. 1 does not react with hydrogen, ethylene, propylene 1,3-butadiene, or hex-1-ene under a variety of conditions.

Experimental Section

All reactions were performed under nitrogen. Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium benzophenone under nitrogen before use. $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (1) was prepared as previously described.[15] Proton and phosphorus nuclear magnetic resonance spectra were obtained at 90.0 and 32.384 MHz, respectively, on Varian EM-390 (^1H) and FT-80 (^{31}P) machines. Proton chemical shifts are reported in δ units (Me_4Si, δ 0.0); phosphorus chemical shifts are relative to 85% H_3PO_4; positive values are to high frequency in both cases.

---

[1] Hayter, R. G. *Inorg. Chem.* **1964**, *3*, 711.
[2] Jarvis, J. A. J.; Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1970**, 1867.
[3] Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499.
[4] Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1358.
[5] Nobile, C. F.; Vasapollo, G.; Giannoccaro, P.; Sacco, A. *Inorg. Chim. Acta* **1981**, *48*, 261.
[6] Heiber, W.; Neumair, G. *Z. Anorg. Allg. Chem.* **1966**, *342*, 93.
[7] Hayter, R. G.; Williams, L. F. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1977.
[8] Coleman, J. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 542.
[9] Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031.
[10] Dobbie, R. C.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 1881.
[11] Abel, E. W.; McLean, R. A. N.; Sabherwal, I. H. *J. Chem. Soc. A* **1968**, 2371.
[12] Issleib, K.; Fröhlich, H. O.; Wenschuh, E. *Chem. Ber.* **1962**, *95*, 2742.
[13] Issleib, K.; Rettkowski, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1966**, *21*, 999.
[14] Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.
[15] Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Rogers, R. D. *Organometallics* **1982**, *1*, 1721.
[16] Jones, R. A.; Atwood, J. L.; Hunter, W. E.; Wright, T. C. *Inorg. Chem.* **1983**, *22*, 993.

0276-7333/83/2302-0874$01.50/0

Spectra were obtained in benzene-d_6 solution at ambient temperature. IR spectra were run on a Perkin-Elmer 1330 spectrophotometer. Nujol mulls were run by using KBr plates.

[Ni(μ-*t*-Bu$_2$P)(PEt$_3$)]$_2$ (2) and [Ni(μ-*t*-Bu$_2$P)(P(OMe)$_3$)]$_2$ (3). PEt$_3$ (0.20 mL, 1.35 mmol) or P(OMe)$_3$ (0.20 mL, 1.69 mmol) was added to [Ni(μ-*t*-Bu$_2$P)(PMe$_3$)]$_2$ (1) (0.20 g, 0.35 mmol) in benzene at room temperature. The solutions were stirred (1 h) and evaporated to dryness under vacuum. The residues were extracted into hexane (25 mL) and the solutions filtered and evaporated to ca. 10 mL. Cooling (–20 °C) yielded red-brown crystals of **2** or **3** which were collected and dried under vacuum: yields 0.18 g (80%) (**2**), 0.18 g (80%) (**3**); mp 202–208 °C dec (**2**), mp 200–207 °C dec (**3**).

Spectroscopic data for **2**: IR (Nujol) 1425 (w), 1355 (w), 1260 (s), 1170 (w), 1140 (w), 1090 (s), 1050 (s), 1000 (w), 800 (s), 760 (s), 730 (w), 710 (w) cm^{-1}; ^{1}H NMR δ 0.90 (6 H, br, PCH_2CH$_3$), 0.14 (9 H, br m, PCH$_2$$CH_3$), 0.48 (18 H, m, *t*-Bu$_2$P); ^{31}P{^{1}H} NMR δ 161.75 (t, *t*-Bu$_2$P), 10.57 (t, PEt$_3$, $^2J_{P-P}$ = 32.5 Hz).

Spectroscopic data for **3**: IR (Nujol) 1230 (m), 1120 (m), 1030 (s), 940 (w), 920 (w), 850 (m), 820 (m), 725 (m), 665 (w) cm^{-1}; ^{1}H NMR δ 2.8 (9 H, br m, POCH$_3$), 0.65 (18 H, br m, *t*-Bu$_2$P); ^{31}P{^{1}H} NMR δ 193.19 (t, *t*-Bu$_2$P), 163.87 (t, P(OMe)$_3$, $^2J_{P-P}$ = 44.3 Hz). Anal. Calcd for $Ni_2C_{28}H_{66}P_4$ (**2**): C, 52.1; H, 10.2; P, 19.2. Found: C, 51.9; H, 10.1; P, 18.3. Calcd for $Ni_2C_{22}H_{54}O_6P_4$ (**3**) C, 40.2; H, 8.23; P, 18.9. Found: C, 39.9; H, 8.40; P, 17.9.

(CO)$_2$Ni(μ-P-*t*-Bu$_2$)$_2$Ni(PMe$_3$) (4) and (CO)$_2$Ni(μ-*t*-Bu$_2$P)$_2$Ni(PEt$_3$) (5). Treatment of a hexane solution of **1** (0.3 g, 0.5 mmol in 50 mL) with CO at 1 atm or at 5 atm in a Fischer–Porter bottle for 1 h yielded a yellow-brown solution. This was evaporated to dryness under vacuum and the residue extracted into hexane (20 mL). The solution was filtered and evaporated to 10 mL under vacuum. Cooling (–20 °C) yielded yellow-brown crystals of **4** which were collected and dried under vacuum: yield quantitative: mp 190–195 °C; IR (Nujol) 2000 (s), 1950 (s), 1360 (m), 1351 (m), 1300 (w), 1280 (w), 1262 (s), 1170 (s), 1100 (s), 1018 (s), 945 (m), 942 (m), 870 (w), 805 (s), 720 (w), 670 (w) cm^{-1}, hexane solution (matched KBr cells) ν_{CO} 2000 (s), 1969 (s) cm^{-1}; ^{1}H NMR δ 0.60 (m, overlapping *t*-Bu$_2$P and PMe$_3$ resonances); ^{31}P{^{1}H} NMR δ 269.28 (d, *t*-Bu$_2$P), –16.88 (t, PEt$_3$, $^2J_{P-P}$ = 46.9 Hz); ^{13}C{^{1}H} NMR δ 199.1 (m, ^{13}CO, enriched, at 50.311 MHz). Anal. Calcd for $Ni_2C_{21}H_{45}O_2P_3$: C, 46.7; H, 8.35, P, 17.2. Found: C, 46.5; H, 8.27; P, 16.5.

5 was prepared by using a similar procedure from **2**: yield quantitative; mp 96–105 °C dec; IR (hexane) 1962 (s), 1922 (s) cm^{-1}; ^{1}H NMR δ 0.5 (m, 45 H, overlapping *t*-Bu$_2$P and PCH$_2$$CH_3$ resonances), 0.1 (m, 6 H, PCH_2CH$_3$); ^{31}P{^{1}H} NMR δ 264.33 (d, *t*-Bu$_2$P), 22.99 (t, PEt$_3$, $^2J_{P-P}$ = 43.97 Hz). Anal. Calcd for $Ni_2C_{24}H_{51}O_2P_3$: C, 49.5; H, 8.76; P, 16.0. Found: C, 49.1; H, 8.80; P, 15.5.

5 was also prepared from **4** as follows. PEt$_3$ (0.487 mmol, 1.25 mL) was added to a solution of **4** (0.066 g, 0.121 mmol) in hexane (10 mL) and the solution stirred for 2.5 h. Volatile materials were removed under vacuum, and the residue was extracted into hexane (5 mL). The solution was filtered and cooled to –20 °C, to yield **5** quantitatively.

4 was prepared from **6** by interaction with 1 equiv of PMe$_3$ in hexane at room temperature (24 h). The solution was worked up and **4** crystallized as above.

1 did not react with H$_2$ (67 atm), ethylene, propylene, or 1,3-butadiene (all at 1 atm). Reaction with NO (1 atm) resulted in a dark brown intractable tar.

Ni$_2$(μ-*t*-Bu$_2$P)$_2$(CO)$_3$ (6). A solution of **1** (0.52 g, 0.94 mmol) in hexane (50 mL) was added to a solution of Mn$_2$(CO)$_{10}$ (0.37 g, 01.94 mmol, hexane, 20 mL) in a quartz Schlenk tube at room temperature. The resultant yellow-brown solution was stirred rapidly and photolyzed (24 h) with a 550-Watt Hanovia mercury vapor lamp. The solution was a slightly paler color after photolysis. Volatile materials were removed under vacuum, the residue was extracted into hexane (2 × 20 mL), and the solution was filtered. The solution was reduced to 20 mL in volume and then cooled to –20 °C. The brown crystals of **6** were collected and dried under vacuum. Also produced was a yellow crystalline material (ca. 30% yield) which was separated manually. This is still under investigation. **6**: yield 0.25 g (54%); mp 153–160 °C dec; IR (hexane) 2020 (m), 2002 (s), 1994 (s), cm^{-1}; ^{1}H NMR δ 0.51 (t, apparent coupling constant J_{P-H} = 13.5 Hz); ^{31}P{^{1}H} NMR δ 312.52 (s). Anal. Calcd for $Ni_2C_{19}H_{36}O_3P_2$: C, 46.4; H, 7.3; P, 12.6. Found: C, 45.9; H, 7.2; P, 11.8.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 4 and 6

	Ni$_2$(μ-*t*-Bu$_2$P)-(CO)$_2$(PMe$_3$) (4)	Ni$_2$(μ-*t*-Bu$_2$P)$_2$-(CO)$_3$ (6)
mol wt	539.97	491.89
space group	$P2_1/n$	$P2_1/n$
cell const		
a, Å	8.673 (4)	12.551 (5)
b, Å	18.589 (8)	13.209 (6)
c, Å	17.828 (8)	16.016 (7)
β, deg	96.45 (2)	108.98 (3)
cell vol, Å^3	2856.2 (5)	2510.9 (5)
molecules/unit cell	4	
D_{calcd}, g cm^{-3}	1.26	1.30
μ(calcd), cm^{-1}	14.93	16.35
radiation, Å	Mo Kα (0.710 69)	
max cryst dimens, mm	0.15 × 0.25 × 0.40	0.20 × 0.25 × 0.35
std reflctns	(200), (040), (008)	(400), (004)
variation of stds	±2%	±2%
reflctns measd	2171	2488
2θ range, deg	$\leqslant$36	$\leqslant$40
reflctns obsd ($I > 3\sigma(I)$)	1656	1610
no. of parameters varied	253	235
goodness of fit (GOF)	2.82	2.60
R	0.050	0.048
R_w	0.055	0.057

X-ray Crystallography. Crystals of both **4** and **6** decompose in ca. 0.5 h when exposed to air. Suitable crystals of **4** or **6** were sealed under vaccum in thin-walled glass capillaries (0.5 mm). Final lattice parameters were determined from 15 high angle reflections (2θ > 40°) carefully centered on an Enraf-Nonius CAD-4 diffractometer. Data were collected at 21 °C by the $\omega/2\theta$ scan technique using graphite-monochromated Mo Kα radiation as previously described.[17] Both space groups were uniquely defined by systematic absences to be $P2_1/n$.

A summary of the data collection parameters is given in Table I. The intensities of 1656 observed (2171 measured) reflections for **4** and 1610 observed (2488 measured) reflections for **6** were corrected for Lorentz and polarization effects but not for absorption. Calculations were carried out with the SHELX system of computer programs.[18] Both structures were solved by the application of the direct method program MULTAN.[19] Least-squares refinement with isotropic thermal parameters led to $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.080 (**4**) and 0.090 (**6**). Hydrogen atoms were not located, and the non-hydrogen atoms were refined with anisotropic thermal parameters to given final values of R = 0.050 for **4** and 0.048 for **6** and $R_w = \{\sum w(F_o - F_c)^2/\sum w(F_o)^2\}^{1/2}$ = 0.055 (**4**) and 0.057 (**6**). Final difference Fourier maps showed no features greater than 0.3 e/Å^3 (**4**) or 0.4 e/Å^3 (**6**). Unit weights were used at all stages of both refinements. The packing diagrams are typical for compounds of this type. This positional parameters for **4** are given in Table II and those for **6** in Table III. Selected bond lengths and angles are collected in Tables IV and V (for **4** and **6**, respectively) and the temperature factors are available elsewhere.[20]

Results and Discussion

The interaction of 2 equiv of lithium di-*tert*-butyl phosphide (Li-*t*-Bu$_2$P) with NiCl$_2$(PMe$_3$)$_2$ in THF at low temperature results in the formation of the nickel(I)

---

(17) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 46.

(18) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

(19) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(20) See paragraph at end of paper regarding supplementary material.

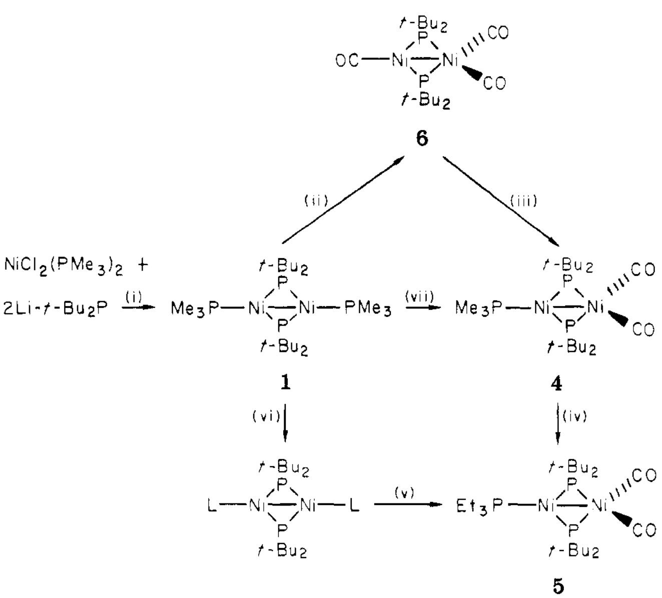
Table II. Final Fractional Coordinates for $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_2(PMe_3)$ (4)

atom	*x/a*	*y/b*	*z/c*	*U*(eqv), Å^2
Ni(1)	0.3436 (1)	0.22742 (7)	0.67353 (8)	0.050
Ni(2)	0.4551 (2)	0.20282 (7)	0.55608 (8)	0.054
P(1)	0.3892 (3)	0.3129 (2)	0.5958 (2)	0.053
C(1)	0.558 (1)	0.3791 (6)	0.6172 (7)	0.073
C(2)	0.676 (1)	0.3392 (7)	0.6767 (8)	0.090
C(3)	0.638 (1)	0.3972 (7)	0.5457 (8)	0.097
C(4)	0.504 (2)	0.4495 (7)	0.6540 (9)	0.118
C(5)	0.219 (1)	0.3598 (7)	0.5377 (7)	0.075
C(6)	0.085 (1)	0.3024 (7)	0.5308 (7)	0.083
C(7)	0.258 (2)	0.3794 (9)	0.4565 (8)	0.114
C(8)	0.159 (2)	0.4267 (7)	0.5796 (9)	0.118
P(2)	0.4005 (3)	0.1211 (2)	0.6414 (2)	0.053
C(9)	0.573 (1)	0.0741 (6)	0.6990 (7)	0.070
C(10)	0.522 (2)	0.0295 (8)	0.7652 (7)	0.100
C(11)	0.665 (1)	0.0258 (8)	0.6469 (8)	0.105
C(12)	0.682 (1)	0.1354 (7)	0.7315 (7)	0.088
C(13)	0.239 (1)	0.0532 (6)	0.6126 (7)	0.072
C(14)	0.109 (1)	0.0984 (8)	0.5676 (9)	0.121
C(15)	0.170 (2)	0.0231 (8)	0.6835 (8)	0.116
C(16)	0.295 (2)	−0.0082 (8)	0.5649 (9)	0.124
P(3)	0.2523 (4)	0.2471 (2)	0.7767 (2)	0.076
C(19)	0.382 (2)	0.301 (1)	0.8453 (9)	0.154
C(20)	0.076 (2)	0.300 (1)	0.771 (1)	0.200
C(21)	0.212 (3)	0.1741 (9)	0.8400 (9)	0.176
C(17)	0.356 (2)	0.1846 (7)	0.4667 (8)	0.079
O(1)	0.300 (1)	0.1724 (6)	0.4069 (6)	0.124
C(18)	0.657 (2)	0.1988 (7)	0.5454 (7)	0.079
O(2)	0.783 (1)	0.1947 (5)	0.5345 (6)	0.118

Table III. Final Fractional Coordinates for $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2(CO)_3$

atom	*x/a*	*y/b*	*z/c*
Ni(1)	0.7457 (1)	0.8271 (1)	0.01658 (8)
Ni(2)	0.6786 (1)	0.6803 (1)	−0.07516 (7)
P(1)	0.8183 (2)	0.7817 (2)	−0.0829 (2)
P(2)	0.6123 (2)	0.7324 (2)	0.0308 (2)
O(1)	0.8206 (8)	0.9980 (7)	0.1280 (6)
O(2)	0.7586 (7)	0.4725 (7)	−0.0498 (6)
O(3)	0.4972 (7)	0.6746 (7)	−0.2444 (5)
C(1)	0.7917 (9)	0.9290 (9)	0.0834 (7)
C(2)	0.7290 (9)	0.5550 (9)	−0.0560 (7)
C(3)	0.5667 (9)	0.6810 (8)	−0.1792 (8)
C(4)	0.9671 (9)	0.7298 (9)	−0.0435 (8)
C(5)	0.987 (1)	0.652 (1)	−0.1106 (9)
C(6)	1.054 (1)	0.816 (1)	−0.020 (1)
C(7)	0.9778 (9)	0.670 (1)	0.0422 (7)
C(8)	0.790 (1)	0.8615 (9)	−0.1872 (7)
C(9)	0.675 (1)	0.913 (1)	−0.2035 (9)
C(10)	0.782 (1)	0.793 (1)	−0.2672 (8)
C(11)	0.881 (1)	0.942 (1)	−0.177 (1)
C(12)	0.6429 (9)	0.6583 (8)	0.1378 (6)
C(13)	0.550 (1)	0.579 (1)	0.1323 (8)
C(14)	0.658 (1)	0.731 (1)	0.2165 (7)
C(15)	0.757 (1)	0.606 (1)	0.1548 (8)
C(16)	0.4644 (8)	0.7866 (8)	−0.0065 (7)
C(17)	0.465 (1)	0.8706 (9)	−0.0753 (7)
C(18)	0.375 (1)	0.703 (1)	−0.0515 (9)
C(19)	0.436 (1)	0.840 (1)	0.0715 (8)

Scheme I



Conditions: (i) THF, −78 °C; (ii) $Mn_2(CO)_{10}$, THF, uv; (iii) PMe_3, hexane; (iv) PEt_3, hexane; (v) CO, 1 atm; (vi) L + PEt_3 (2), $P(OMe_3)_3$ (3); (vii) CO, 1 atm.

phosphide $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (1) in yields of ca. 50% (eq 1) (see Scheme I). We have been unable to identify

$$NiCl_2(PMe_3)_2 + 2Li\text{-}t\text{-}Bu_2P \xrightarrow[-78\ ^\circ C]{THF} [Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2 + \text{other products} \quad (1)$$

or characterize any other products from the reaction mixtures. The structure of 1 as revealed by X-ray crystallography has two nickel(I) atoms linked by a single metal–metal bond (Ni–Ni = 2.375 (3) Å) and bridged by two $t\text{-}Bu_2P$ groups.[15] The nickel–nickel bond appears to be a feature which is retained in the chemistry of the $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2$ core. A single PMe_3 ligand is attached to each nickel atom such that the $Me_3P\text{-}Ni\text{-}Ni\text{-}PMe_3$ unit is linear. The structure of $[Ni(\mu\text{-}(SiMe_3)_2P)(PR_3)]_2$, recently determined, is similar although full structural details are not yet available for comparison (see ref 23). Both metals have low formal coordination numbers and electron counts of 16 (including a single metal–metal bond), and we have investigated their reactions with a number of Lewis bases.

Phosphine Substitution. $^{31}P\{^1H\}$ NMR data in toluene solution show that in the presence of excess PMe_3 1 undergoes exchange between free and coordinated PMe_3. At room temperature the triplet–triplet pattern of 1 (δ 171.03 (t, $t\text{-}Bu_2P$), 23.11 (t, PMe_3, $^2J_{P-P}$ = 30.0 Hz)) is replaced by two sharp singlets at δ 169.33 and 22.45 in addition to a resonance for free PMe_3 (δ −62.9). When the solution is cooled to −60 °C, the resonances broaden slightly. At −92 °C the exchange is sufficiently slow on the NMR time

Table IV. Key Bond Lengths (Å) and Angles (deg) for 4

Bond Distances

Ni(1)–Ni(2)	2.446 (2)	C(18)–O(2)	1.14 (1)	Ni(2)–C(18)	1.78 (1)
Ni(1)–P(2)	2.131 (3)	Ni(1)–P(1)	2.173 (3)	Ni(2)–P(1)	2.260 (3)
Ni(2)–C(17)	1.75 (1)	Ni(1)–P(3)	2.115 (4)	C(17)–O(1)	1.15 (1)
P(1)–C(1)	1.92 (1)	Ni(2)–P(2)	2.238 (3)		

Bond Angles

P(1)–Ni(1)–P(2)	116.3 (1)	Ni(1)–P(1)–C(1)	122.1 (4)	P(2)–Ni(2)–C(17)	111.6 (4)
P(2)–Ni(1)–P(3)	121.0 (1)	Ni(1)–P(3)–C(20)	116.0 (6)	P(2)–Ni(2)–C(18)	109.2 (4)
P(1)–Ni(2)–C(17)	110.1 (4)	Ni(2)–C(18)–O(2)	176 (1)	Ni(1)–P(1)–Ni(2)	66.9 (1)
P(1)–Ni(2)–C(18)	110.9 (4)	P(1)–Ni(1)–P(3)	122.7 (1)	Ni(1)–P(2)–Ni(2)	68.0 (1)
C(17)–Ni(2)–C(18)	106.2 (6)	P(1)–Ni(2)–P(2)	108.7 (1)	Ni(2)–C(17)–O(1)	176 (1)

Table V. Key Bond Lengths (Å) and Angles (deg) for 6

Bond Distances

Ni(1)-Ni(2)	2.414 (2)	P(1)-C(4)	1.89 (1)	Ni(1)-P(1)	2.162 (3)
Ni(1)-P(2)	2.160 (3)	C(1)-O(1)	1.14 (1)	Ni(1)-C(1)	1.70 (1)
Ni(2)-P(1)	2.242 (3)	C(3)-O(3)	1.13 (1)	Ni(2)-P(2)	2.228 (3)
Ni(2)-C(2)	1.76 (1)	C(2)-O(2)	1.15 (1)	Ni(2)-C(3)	1.80 (1)

Bond Angles

P(1)-Ni(1)-P(1)	116.4 (1)	C(2)-Ni(2)-C(3)	107.1 (5)	P(2)-Ni(2)-C(2)	111.0 (3)
P(2)-Ni(1)-C(1)	120.6 (4)	Ni(1)-P(1)-C(4)	117.5 (4)	P(2)-Ni(2)-C(3)	109.4 (3)
P(1)-Ni(2)-C(2)	109.1 (3)	P(1)-Ni(1)-C(1)	123.0 (4)	Ni(1)-P(1)-Ni(2)	66.43 (9)
P(1)-Ni(2)-C(3)	109.6 (3)	P(1)-Ni(2)-P(2)	110.5 (1)	Ni(1)-P(2)-Ni(2)	66.71 (9)

scale for phosphorus–phosphorus coupling constants to be observed. At this temperature the A_2X_2 pattern for 1 is observed (δ 170.05 (t, *t*-Bu$_2$*P*), 22.68 (t, PMe$_3$, $^2J_{PP}$ = 30.52 Hz)). Thus, although 1 will exchange PMe$_3$ ligands in solution, no new species such as a tris- or tetrakis(phosphine) complex can be detected. Pure 1 may be recovered in high yield from these solutions following evaporation to dryness and recrystallization from hexane.

Both PMe$_3$ ligands of 1 are readily replaced by interaction with excess PEt$_3$ or P(OMe)$_3$ (see Scheme I). The new complexes [Ni(μ-*t*-Bu$_2$P)(L)]$_2$ (L = PEt$_3$ (2), P(OMe)$_3$ (3)) are isostructural with 1 on the basis of NMR data (see Experimental Section). The complex [Ni(μ-Ph$_2$P)]$_2$(PEt$_3$)$_3$[3] (6) which probably has an asymmetric structure containing two PEt$_3$ ligands bonded to one nickel atom is known, but the diphenylphosphido bridges no doubt cause very little steric hindrance at terminal sites. In contrast space-filling model studies show that the *tert*-butyl groups of the *t*-Bu$_2$P units which we have employed would hinder the coordination of two phosphines to each end of the dinuclear unit. In support of this we have also recently synthesized and structurally characterized the complex [Ni(μ-*t*-BuHP)(PMe$_3$)$_2$]$_2$ which has two μ-*t*-BuHP bridges and a planar Ni$_2$P$_2$ core, similar to that in 1. In this complex the less sterically demanding μ-*t*-BuHP groups permit each nickel atom to coordinate two PMe$_3$ ligands.[21] In this complex each nickel has a distorted tetrahedral coordination geometry.

Reaction with CO. Since the tetracarbonyl complex [Ni(μ-Ph$_2$P)(CO)$_2$]$_2$ is known,[1,2] we attempted the synthesis of the μ-*t*-Bu$_2$P analogue by treatment of 1 or 2 with CO. However, unlike the reaction with phosphines the interaction of either 1 or 2 with CO (1 or 40 atm) does not result in the simple replacement of both phosphine groups. Instead one phosphine is replaced by two CO ligands while the other remains attached to give (CO)$_2$Ni(μ-*t*-Bu$_2$P)$_2$Ni(PR$_3$) (4, 5) in high yields. They are yellow-brown, diamagnetic, and crystalline. Spectroscopic data is in accord with the structure of 4 as determined by X-ray crystallography. For 4 the IR spectrum has terminal ν_{CO} bands at 2000 (s), 1950 (s) cm^{-1}, and the $^{31}P\{^1H\}$ NMR spectrum is the expected A_2X pattern. Data for 5 are similar. A view of the molecule of 4 is presented in Figure 1. The carbonyls lie in a plane perpendicular to the central Ni$_2$P$_2$ core giving Ni(2) a distorted tetrahedral geometry. The Ni–Ni distance (2.446 (2) Å) is consistent with the retention of a single metal–metal bond with electron counts of 18 (Ni(2)) and 16 (Ni(1)).

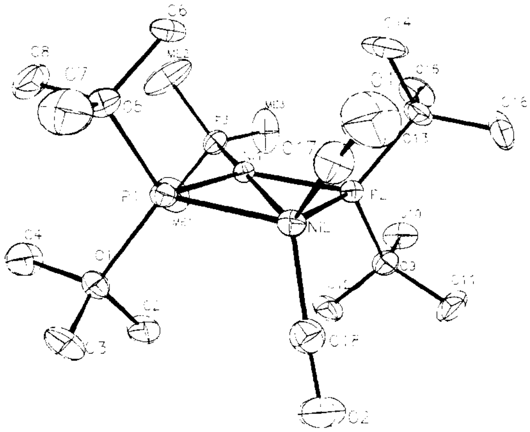


Figure 1. View of the molecule Ni$_2$(μ-*t*-Bu$_2$P)$_2$(CO)$_2$(PMe$_3$) (4).

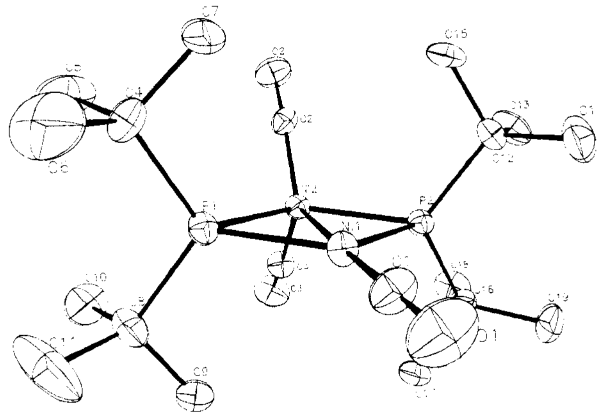


Figure 2. View of the molecule Ni$_2$(μ-*t*-Bu$_2$P)$_2$(CO)$_3$ (6).

As for 1, $^{31}P\{^1H\}$ NMR data in toluene solution show that in the presence of excess PMe$_3$ 4 undergoes exchange between free and coordinated PMe$_3$. The CO ligands are not replaced since 4 can be recovered unchanged after treatment (10 h) with a tenfold excess of phosphine in benzene. At room temperature $^{31}P\{^1H\}$ NMR spectra (in the presence of excess PMe$_3$) show two broad singlets that replace the A_2X triplet–doublet pattern of pure 4. The resonances sharpen on cooling, and the X_2X pattern is restored at −90 °C (δ 268.90 (d, μ-*t*-Bu$_2$P, 13.12 (t, PMe$_3$, $^2J_{PP}$ = 46.7 Hz)). Reaction of 4 with excess PEt$_3$ gives 5 in high yield. Since all these reactions take place in homogeneous solutions the isolation of products can not be a function of solubility. The reason why the CO substitution reaction of 1 to give 4 appears to stop halfway is at present not clear. We are currently studying the kinetics of these reactions in order to gain further mechanistic information.

Reaction with Mn$_2$(CO)$_{10}$: Ni$_2$(μ-*t*-Bu$_2$P)$_2$(CO)$_3$ (6). The unusual asymmetric substitution pattern for 4 and 5 that is also probably present in Ni$_2$(μ-Ph$_2$P)$_2$(PEt$_3$)$_3$[3] appears again in the product of the reaction of 1 with Mn$_2$(CO)$_{10}$. There is no reaction on mixing equimolar amounts of 1 and Mn$_2$(CO)$_{10}$ in THF at room temperature (24 h). However, after photolysis the nickel-containing product Ni$_2$(μ-*t*-Bu$_2$P)$_2$(CO)$_3$ (6) can be isolated in ca. 50% yield. This is diamagnetic, red-brown, and crystalline and is readily recrystallized from hexane. The spectroscopic data are consistent with the structure as determined by X-ray crystallography (see Experimental Section). A view

---

[21] Jones, R. A.; Seeberger, M. H., manuscript in preparation.

Organometallics 1983, 2, 878-882

of the molecule is shown in Figure 2. The structure is similar to that of 4 with the PMe_3 group of 4 now replaced by CO. In this reaction the $Mn_2(CO)_{10}$ no doubt acts as a phosphine "sink" and permits the $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2$ core to be attacked by CO present in solution. As noted above the tetracarbonyl complex $[Ni(\mu\text{-}Ph_2P)(CO)_2]_2$ is a known, stable species. However 6 does not react with further CO and can be recovered unchanged after exposure to CO (5 atm). IR and ^1H and ^{13}C NMR spectra under CO (1 atm) also show no change at room temperature and at −80 °C. However, replacement of one CO in 6 is possible with PMe_3 which yields 4 in high yield. At present we have no rationale to account for the asymmetric substitution patterns observed nor for the failure to form a tetracarbonyl complex by reaction of 6 with CO. Steric factors are probably not a major factor in the latter case since we have recently synthesized and characterized the cobalt complex $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ which is quite stable and has two pseudotetrahedral Co atoms.[22]

Lastly, it has been noted by several groups of workers that the ^{31}P NMR resonances for bridging μ-PPh_2 ligands can be correlated with M–P–M bond angles and M–M bond distances. Low-field (50–200 ppm) resonances are associated with short (i.e., bonding) M–M distances and acute M–P–M angles. For the three Ni(I) di-*tert*-butylphosphido dimers which we have structurally characterized 1, 4, and 6, the geometry of the M_2P_2 cores are very similar (Ni–Ni = ca. 2.4 Å, Ni–P–Ni = ca. 66°). However, the $^{31}P\{^1H\}$ NMR chemical shifts for the bridging phosphido phosphorus atoms cover a considerable downfield range ((1) δ 171, (4) δ 269, (6) δ 312.52). The downfield shift increases with increasing numbers of carbonyls on the central $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2$ core. The trend may therefore be due to increased deshielding of the phosphorus nuclei by the CO ligands since they are better π acceptors than PMe_3 ligands. Further studies are in progress.

Acknowledgment. We thank the Dow Chemical Co. Midland, MI, the Robert A. Welch Foundation, the University Research Institute (University of Texas at Austin) (R.A.J.), and the National Science Foundation (J.L.A. and R.A.J.) for financial support.

Registry No. 1, 82808-29-5; 2, 85318-51-0; 3, 85318-52-1; 4, 85318-53-2; 5, 85318-54-3; 6, 85318-55-4; $Mn_2(CO)_{10}$, 10170-69-1; Ni, 7440-02-0.

Supplementary Material Available: Tables of thermal parameters, complete bond lengths and angles, and structure factors for 4 and 6 (24 pages). Ordering information is given on any current masthead page.

---

[22] Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics*, submitted for publication.

[23] **Note Added in Proof**: The structure has recently been published, see: Deppisch, Von. B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1982**, *490*, 129.

Crystal Structures of (μ-Trithio)bis[tricyclohexylgermanium(IV)] and (μ-Trithio)bis[triphenylgermanium(IV)]

François Brisse,* Micheline Vanier, Marc J. Olivier, Yves Gareau, and Kosta Steliou

Département de Chimie, Université de Montréal, C.P. 6210, Succursale A,
Montréal, Québec, H3C 3V1 Canada

Received September 9, 1982

Crystals of (μ-trithio)bis[tricyclohexylgermanium(IV)], $[(C_6H_{11})_3Ge]_2S_3$ (I), belong to the triclinic system of space group $P1$. The unit cell has the following dimensions: a = 9.004 (7) Å, b = 9.808 (4) Å, c = 11.815 (5) Å, α = 83.14 (3)°, β = 84.64 (5)°, γ = 66.92 (5)°, V = 951.8 Å^3, Z = 1, d_{calcd} = 1.291 Mg m^{-3}, $F(000)$ = 394, Cu Kα radiation, μ(Cu Kα) = 3.59 mm^{-1}. The structure, solved by direct methods, was refined by least squares to a final R value of 0.063 for 3185 observed reflections. $[(C_6H_5)_3Ge]_2S_3$ (II), (μ-trithio)bis[triphenylgermanium(IV)], is monoclinic of space group $P2_1/n$. The unit cell has the following dimensions: a = 11.969 (5) Å, b = 17.982 (6) Å, c = 16.741 (9) Å, β = 100.37 (4)°, V = 3543.9 Å^3, d_{calcd} = 1.319 Mg m^{-3}, Z = 4, $F(000)$ = 1432, Mo Kα radiation, μ(Mo Kα) = 1.864 mm^{-1}. The least-squares refinement of the atomic coordinates and temperature factors was concluded when R reached 0.096 for 1435 observed reflections. Both structures consist of a Ge–S–S–S–Ge sequence, in a coiled-type conformation, at the ends of which are bonded three cyclohexyl groups (I) or three phenyl groups (II). The two torsion angles describing the Ge–S–S–S–Ge part are both equal to 100.2 (3)° in I and to −96 (1) and −104 (1)° in II. The S–S, S–Ge, and Ge–C distances respectively have average values of 2.009, 2.282, and 1.976 Å in I and 2.023, 2.260, and 1.90 Å in II. The S–S–S angle is 111.3 (3)° in I and 107.5 (7)° in II while S–S–Ge average 105.0° in I and 103.1° in II. Around Ge, the S–Ge–C and C–Ge–C angles have mean values of 106.7 and 112.1°, respectively, for I and 107.6 and 111.4°, respectively, for II. The substituents on Ge have a propeller-like arrangement. Looking down the Ge–Ge direction they adopt a staggered disposition.

Introduction

As part of our continuing interest in the synthetic utility of group 4 metal-protected mercaptides,[1] we have prepared some phenyl- and cyclohexyl-substituted germanium(IV) polysulfides whose crystal structures have been established by X-ray analysis. This study has led us to some interesting observations concerning the substituent conformation about the sulfur sequence. For example, the dihedral angle between the sulfur substituents in most nonchelated carbon-bonded disulfides is known[2] to have values in the

---

[1] Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.

[2] Rindorf, G.; Jørgensen, F. S.; Snyder, J. P. *J. Org. Chem.* **1980**, *45*, 1015.

0276-7333/83/2302-0878$01.50/0 © 1983 American Chemical Society