tance at the expense of a copper–ruthenium bond certainly seems consistent with the presence of an attractive copper–copper interaction.

Since there exists no thermodynamic data for copper–ruthenium bond strengths in molecular species, it is difficult to explain convincingly the geometry adopted by the cluster. Indeed any explanation based purely upon comparisons between Cu–Ru and Cu–Cu bond energies will have to accommodate the structure of a related copper–ruthenium cluster, (toluene)$_2$Cu$_2$Ru$_6$(CO)$_{18}$, in which the two copper atoms cap opposite faces of the Ru$_6$ octahedral core.[19]

Acknowledgment. We wish to thank Dr. J. Johnson and Dr. G. Doyle of Exxon Research and Engineering Co., for fruitful discussions, and to acknowledge helpful discussions with the late Professor P. Chini and for data on the Cu$_2$Rh$_6$ system prior to publication.

Registry No. 1, 73413-28-2; 2, 80679-05-6; Cu(CH$_3$CN)$_4$BF$_4$, 15418-29-8.

Supplementary Material Available: Tables of general temperature factor expressions and of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

Communications

Synthesis and Characterization of an Exceptionally Air-Stable Organometallic Nickel(II) Complex of the Organolithium Reagent $(C_6H_5)_2P(S)CH_2Li$. The X-ray Crystal Structure of Chloro(triphenylphosphine)[diphenyl(methylene)phosphoranylthio-*S*,*C*]nickel(II), $\overline{\mathrm{NiCH_2P(S}}\mathrm{)Ph_2(PPh_3)Cl}$

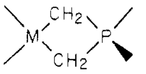
Anthony M. Mazany and John P. Fackler, Jr.*

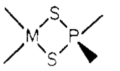
Department of Chemistry, Case Institute of Technology
Case Western University
Cleveland, Ohio 44106

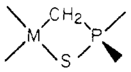
Received December 1, 1981

Summary: The synthesis and single-crystal X-ray structure of an organometallic complex of nickel(II) formed from the lithium reagent LiCH$_2$P(S)Ph$_2$, Ni(mtp)(PPh$_3$)Cl, are described.

Ylides coordinate to metal ions both as monodentate and bidentate ligands.[1,2] The bidentate coordination of phosphorus ylide anions I is analogous to coordination by


I


II


III

phosphoranyldithioate ligands II. The phosphoranyldithioates are found to have many important properties.[3] In view of the nearly identical electronegativities[4] of carbon and sulfur we were intrigued with the possibility that the anion CH$_2$P(S)R$_2^-$ might function as an organometallic chelate, bonding to metals through both carbon and sulfur. Furthermore, M–S bond lability[5] suggested that organometallic products of type III might display some interest in new organometallic chemistry.

Seyferth and co-workers[6,7] have shown that phosphine oxides and sulfides react with methyllithium to yield LiCH$_2$P(X)(C$_6$H$_5$)$_2$, X = S and O. The lithium methylenethiophosphinate, Li(mtp), reacts readily with metal halide species, and, in the case of (Ph$_3$P)$_2$NiCl$_2$, the reaction product NiCH$_2$P(S)Ph$_2$(PPh$_3$)Cl,Ni(mtp)(PPh$_3$)Cl, has been characterized by X-ray crystallography. This compound is the first member of an ostensibly, rather large class of new sulfur-containing transition-metal organometallic species. The nickel(II) complex shows exceptional stability to reaction with air.

Preparation. Methyllithium (ca. 1.2 M in diethyl ether) is added dropwise to 1 equiv of triphenylphosphine sulfide in a 1:2 THF–Et$_2$O solution under nitrogen. The resulting amber solution is stirred for 1 h, and 1 equiv of NiCl$_2$(PPh$_3$)$_2$ is added directly to the reaction mixture. A red precipitate forms immediately, although stirring is continued for 24 h. The yield is 75%. The precipitate initially was removed by filtration under nitrogen but subsequently was found to be stable in air. Repeated recrystallization from CH$_2$Cl$_2$ and washing with acetone produces bright red orthorhombic crystals, mp ca. 140 °C dec. Anal. Calcd for NiC$_{31}$H$_{27}$P$_2$SCl: C, 63.35; H, 4.63%. Found: C, 63.24; H, 4.87%.

Results and Discussion. The Ni(mtp)(PPh$_3$)Cl is soluble in dichloromethane and tetrahydrofuran; however, only the dichloromethane solutions are stable in air for more than a few minutes. The infrared spectrum exhibits weak methylene vibrations at 2920 and 2840 cm^{-1}, in addition to the peaks arising from the phosphine and mtp phenyl groups. The ^{1}H NMR spectra for the diamagnetic material in CD$_2$Cl$_2$ at ambient temperature shows a broad resonance at δ −0.56 which is assigned to the methylene protons. A doublet $^2J_{PCH} \approx 10$ Hz is observed at temperatures below −20 °C in CDCl$_3$. Several peaks are found in the phenyl region (δ 7.3–7.7). The methylene proton resonance shows that the complex is fluxional in solution. Mixed ligand dithiolate complexes of nickel(II) generally are fluxional.[8] In this case either Ni–S or Ni–C bond rupture (or both) may occur with a low activation energy (less than 40 kJ/mol).

While spectroscopic studies were ambiguous with regard to the structure of Ni(mtp)(PPh$_3$)Cl, the X-ray crystal structure is not. Standard crystallographic procedures[9]

---

[1] Schmidbaur, H. *Acc. Chem. Res.* **1975,** *8,* 62.

[2] Stein, J.; Fackler, J. P., Jr.; Paparizos, C.; Chen, H.-W. *J. Am. Chem. Soc.* **1981,** *103,* 2192–2198.

[3] Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973,** *35,* 65–129.

[4] Cotton, F. A; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980.

[5] Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stephenson, T. A.; Gould, R. O.; Alison, J. M. C.; Fraser, A. J. F. *Inorg. Chem.*, in press.

[6] Seyferth, D.; Welch, D. E. *J. Organomet. Chem.* **1964,** *2,* 1–7.

[7] Seyferth, D.; Welch, D. E.; Herren, J. K. *J. Am. Chem. Soc.* **1963,** *85,* 642–643.

[8] See, for example: Masters, A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **1980,** *39,* 111–118.

0276-7333/82/2301-0752$01.25/0

Table I. Positional, Thermal, and Anisotropic Thermal Parameters for $Ni[CH_2P(S)Ph_2]Cl(PPh_3)$

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C2A	0.6997 (7)	0.6682 (5)	0.0083 (3)	3.7 (2)	C1AA	0.3579 (7)	0.8179 (5)	0.1479 (2)	3.6 (2)
C2B	0.8390 (7)	0.5422 (5)	0.0556 (2)	3.4 (2)	C1AB	0.4050 (7)	0.8237 (5)	0.2179 (2)	3.2 (2)
C2AA	0.6950 (9)	0.7586 (6)	−0.0613 (3)	5.4 (2)	C1AC	0.3075 (8)	0.8830 (5)	0.2232 (3)	4.0 (2)
C2AB	0.6126 (8)	0.6485 (6)	−0.0196 (6)	4.8 (2)	C1AD	0.2627 (8)	0.8769 (5)	0.1541 (3)	4.2 (2)
C2AC	0.6103 (9)	0.6943 (6)	−0.0556 (3)	5.8 (2)	C1AE	0.2400 (8)	0.9085 (5)	0.1909 (3)	4.0 (2)
C2AD	0.7788 (8)	0.7778 (6)	−0.0343 (3)	5.1 (2)	C1BA	0.4841 (8)	0.5973 (5)	0.2260 (3)	4.7 (2)
C2AE	0.7874 (8)	0.7327 (5)	0.0024 (3)	4.6 (2)	C1BB	0.6463 (8)	0.6872 (5)	0.2508 (3)	3.9 (2)
C2BA	0.9473 (9)	0.5687 (5)	0.0736 (3)	5.0 (2)	C1BC	0.4759 (9)	0.5581 (6)	0.2642 (3)	5.7 (2)
C2BB	0.0522 (9)	0.5151 (7)	0.0725 (3)	6.1 (2)	C1BD	0.5573 (8)	0.5831 (6)	0.2935 (3)	4.8 (2)
C2BC	0.0452 (9)	0.4353 (6)	0.0554 (3)	5.2 (2)	C1BE	0.6381 (8)	0.6476 (6)	0.2874 (3)	4.8 (2)
C2BD	0.9389 (9)	0.4092 (6)	0.0381 (3)	5.2 (2)	C1CA	0.8142 (7)	0.7623 (5)	0.1768 (2)	3.6 (2)
C2BE	0.8332 (8)	0.4620 (6)	0.0384 (3)	5.1 (2)	C1CB	0.7785 (8)	0.9310 (5)	0.1551 (3)	4.8 (2)
C1A	0.4296 (6)	0.7908 (4)	0.1798 (2)	2.3 (1)	C1CC	0.8957 (8)	0.8994 (6)	0.1598 (3)	4.8 (2)
C1B	0.5693 (6)	0.6619 (4)	0.2187 (2)	2.6 (1)	C1CD	0.6761 (7)	0.8769 (5)	0.1603 (3)	3.6 (2)
C1C	0.6925 (6)	0.7918 (4)	0.1710 (2)	2.5 (1)	C1CE	0.9134 (8)	0.8164 (6)	0.1716 (3)	4.4 (2)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.54206 (8)	0.63786 (6)	0.11801 (3)	25 (1)	26 (3)	27 (13)	−1 (1)	1 (2)	−1 (3)
P(1)	0.5595 (2)	0.7190 (1)	0.17139 (6)	20 (1)	25 (3)	27 (13)	0 (1)	0 (2)	0 (3)
P(2)	0.7027 (2)	0.6096 (1)	0.05570 (7)	31 (1)	33 (3)	36 (13)	−2 (1)	4 (2)	−3 (3)
S	0.5443 (2)	0.5458 (1)	0.06494 (7)	35 (1)	37 (3)	40 (13)	−5 (1)	4 (2)	−5 (3)
Cl	0.3517 (2)	0.5940 (1)	0.13275 (6)	27 (1)	44 (3)	36 (13)	−4 (1)	1 (2)	0 (3)
C	0.7042 (7)	0.6802 (5)	0.0974 (3)	39 (4)	39 (4)	45 (13)	−6 (2)	9 (2)	−8 (3)

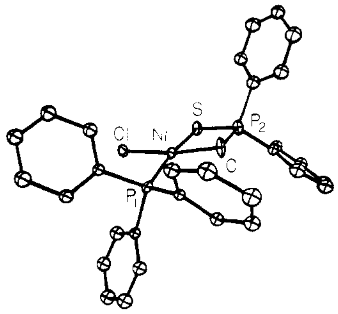


Figure 1. The molecular structure of $Ni[CH_2(S)PPh_2]Cl(PPh_3)$. Bond lengths: Ni–C = 1.999 (8) Å, Ni–S = 2.284 (2) Åa, Ni–P(1) = 2.197 (2) Å, Ni–Cl = 2.216 (2) Å, P(2)–S = 1.999 (3) Å, P(2)–C = 1.776 (8) Å, S⋯CH_2 = 2.922 (8) Å. Bond angles: S–P(2)–CH_2 = 101.3 (3)°, S–Ni–Cl = 89.3 (2)°, Cl–Ni–P(1) = 94.4 (2)°, S–Ni–C = 86.0 (3)°, P(1)–Ni–C = 90.9 (3)°.

yielded $R = 0.070$ and $R_w = 0.071$ for 2817 independent data with Ni, S, Cl, P, and CH_2 carbon atoms refined anisotropically. The structure is presented in Figure 1.

The NiSPCCl atom core of $Ni(mtp)PPh_3Cl$ is nearly planar (root mean square deviation 0.097 Å). The P(2)–CH_2 distance of 1.776 (8) Å is close to the distance observed in other phosphorus ylide complexes.[1,2] The chelate bite distance of 2.922 (8) Å is not unusually short, and consequently the S–Ni–C angle of 86.0 (3)° is only a few degrees smaller than ideal for a square-planar complex. The S–P(2)–CH_2 angle of 101.3 (3)° is the same internal angle as found[10] in $Ni(S_2PPh_2)_2$. In $\{Ni[(CH_2)_2P(CH_3)_2]_2\}$ the internal CH_2–P–CH_2 angle is[11] 97.7°.

The air stability of crystalline $Ni(mtp)(PPh_3)Cl$ is exceptional for an organometallic alkyl complex of nickel(II). Solution reactivity with various solvents, olefins, and other species is being examined. Exploratory studies have shown that other transition-metal complexes of mtp can be synthesized readily. These results will be reported later.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, Grant CHE-8013141, are gratefully acknowledged for support.

Registry No. $Ni(mtp)(PPh_3)Cl$, 80925-78-6; $NiCl_2(PPh_3)_2$, 14264-16-5; triphenylphosphine sulfide, 3878-45-3; methyllithium, 917-54-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

---

[9] Crystal data: $C_{31}H_{27}P_2SClNi$: mol wt 587.74, crystal dimensions of disk ca. 0.2 mm diameter × 0.1 mm thick, orthorhombic, space group *Pbca* (No. 61), $a = 10.672$ (2) Å, $b = 15.617$ (6) Å, $c = 33.425$ (8) Å, $V = 5516$ (3) Å^3, $\rho_{calcd} = 1.40$ g/cm^3, $\rho_{obsd} = 1.40$ (3) g/cm^3, $Z = 8$, μ(Mo Kα) = 10.0 cm^{-1}. Intensity data (5692 reflections, $2.0 \leq 2\theta \leq 55°$, h,k,l) were recorded on a Syntex $P2_1$ four-circle diffractometer at ambient temperature (ca. 22 °C) with graphite-monochromated Mo Kα radiation. The 2870 reflections with $I > 3.0\sigma(I)$ were corrected[12] for Lorentz, decay, and polarization effects (not corrected for absorption—transmission factors range from 0.8 to 0.9). The number of parameters read including phenyl hydrogen atoms was 673, of which 180 were varied. The final difference map contained a peak intensity corresponding to 0.7 e/Å^3.

[10] Porta, P.; Sgamellotti, A.; Vinciguerra, N. *Inorg. Chem.* **1968**, *7*, 2625.

[11] Brauer, D. J.; Kruger, D.; Roberts, P. J.; Tsay, U.-H. *Chem. Ber.* **1974**, *107*, 3706–3715.

[12] See: Chen, H.-W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 22, for a description of crystallographic procedures and computer programs used.

Heteronuclear Organotransition-Metal Clusters: Rational Syntheses and Fluxional Behavior

Gérard Jaouen,*[1a,b] Angela Marinetti,[1b]
Bernard Mentzen,[1c] Robert Mutin,[1c]
Jean-Yves Saillard,[1b] Brian G. Sayer,[1d] and
Michael J. McGlinchey*[1d]

Ecole Nationale Supérieure de Chimie
75231 Paris Cedex 05, France
Laboratoires de Chimie du Solide et
Inorganique Moléculaire, LA254, et
de Chimie des Organométalliques, ERA 477
Université de Rennes I, 35042 Rennes Cedex, France
Institut de Recherche sur la Catalyse
69626 Villeurbanne Cedex, France, and
Department of Chemistry, McMaster University
Hamilton, Ontario, L8S 4M1, Canada

Received December 8, 1981

Summary: Chiral organotransition-metal tetrahedral clusters of the type (RC≡CR′)MM′, where M = $(C_5H_5)Ni$

0276-7333/82/2301-0753$01.25/0