Synthesis and Reactivity of [(Thiomethoxy)methyl]- and [(Dimethylsulfonio)methyl]nickel(II) Complexes

James G. Davidson, E. Kent Barefield,* and Donald G. Van Derveer

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received July 17, 1984

The new complexes [NiCp(L)CH_2SCH_3] (L = PPh_3, $PPhMe_2$, $P(OCH_3)_3$ were prepared by substitution of halide in [NiCp(L)X] and, in the case of L = PPh_3, by reaction of chloromethyl methyl sulfide with [$Ni(PPh_3)_2(C_2H_4)$], to give [$Ni(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)$] or [$Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)$] depending upon reaction conditions, followed by reaction with sodium cyclopentadienide. Addition of ammonium hexafluorophosphate to [$Ni(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)$] in acetone produced [$Ni(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)$]$PF_6$. S-methylation of the cyclopentadienyl complexes yielded the sulfonium ions [$NiCp(L)CH_2S(CH_3)_2$]$^+$. [$NiCp(PPh_3)CH_2S(CH_3)_2$]$^+$ was also prepared from [NiCp(L)X] and dimethylsulfonium methylide, but the dinuclear species {[$NiCp(PPh_3)CH_2$]$_2S(CH_3)$}$^+$ was formed in comparable amounts. The structure of the dinuclear complex (PF_6^- salt, acetone solvate) was determined by a single-crystal X-ray structure: $C_{52}H_{53}F_6Ni_2OP_3S$; space group *Pbcm*; $a = 11.20$ (1) Å, $b = 18.814$ (6) Å, $c = 24.40$ (1) Å; $Z = 4$; $R = 0.11$ and $R_w = 0.096$ for 2100 data with $F > 3\sigma_F$. The sulfur and methyl carbons of the cation lie on a mirror plane. The mononuclear sulfonium salts reacted with charged nucleophiles (X = Br^-, I^-, and CN^-) to produce [NiCp(L)X]. That these reactions occurred by substitution of the $CH_2S(CH_3)_2$ group was suggested by the fact that [$NiCp(PPh_3)CH_2CN$], prepared from the halide and $LiCH_2CN$, was stable under the reaction conditions. The nickelated sulfonium salts were found to have limited utility as reagents for the cyclopropanation of cyclooctene in acetonitrile solution.

Introduction

The work reported here is a result of our continuing interest in α-heteroatom-substituted alkyl complexes and the fact that, in comparison with many other metals, such chemistry is relatively undeveloped for nickel. A secondary reason for undertaking the work was the possibility that other metalated sulfonium salts besides those of iron[1] might be useful as alkylidene transfer agents.

One feature that has lead to the extensive development of α-heteroatom-substituted alkyl chemistry of many metals is their relative ease of preparation by nucleophilic reactions of metalate anions, which are frequently readily available from simple alkali-metal reduction of dinuclear complexes containing metal–metal bonds. Although [NiCp(CO)]$_2$ is known and can apparently be reduced to [NiCp(CO)]$^-$, this species has not been very useful for synthetic purposes. Simple alkyl derivatives have been generated, but only perfluoro derivatives were stable enough to be isolated.[2] Therefore, most NiCp alkyls contain ligands other than CO and other routes to their synthesis are required. In the present case, syntheses of (thiomethoxy)methyl complexes based on oxidative addition of CH_3SCH_2Cl to nickel(0) reagents and substitution by $LiCH_2SCH_3$ in nickel(II) reagents were developed. Sulfonium salts were obtained by S-alkylation of the (thiomethoxy)methyl complexes and, in one case, direct substitution by the ylide $CH_2S(CH_3)_2$. Oxidative addition reactions of CH_3SCH_2Cl had been used earlier by Yoshida[3] for the preparation of [(thioalkoxy)methyl]palladium and -platinum complexes. At the time we began this work only two complexes [$NiCp(PPh_3)CH_2SPh$][4] and {$Fe(PMe_3)_3$(Cl)[CH_2SMe]}[5] had been prepared from $LiCH_2SR$ reagents, and the thermally sensitive methylide $CH_2S(CH_3)_2$ had not been utilized in inorganic synthesis. Subsequently, both Fackler[6] and Booth[7] reported that the methylide could be used for the synthesis of metalated sulfonium salts and Mintz reported some additional uses of $LiCH_2SR$ reagents.[8] In fact, Booth reported the synthesis of {$NiCp(PPh_3)$[$CH_2S(CH_3)_2$]}$^+$, which was one of our target compounds, although his data are in substantial conflict with ours.

Alkylidene transfer to olefins from metal complexes as a route to cyclopropanes is currently of considerable interest. An especially effective class of such reagents has been based on compounds that are thought to be sources of [$FeCp(L)_2CR_2$]$^+$. A variety of such compounds have been studied, but the most successful appear to be the α-ethers {FeCp(CO)(L)[CH(R)(OCH_3)]},[9] in combination with strong electrophiles, and the salts of the sulfonium ions {$FeCp(CO)_2$[$CH(R)SR_2$]}$^+$.[1] Either reagent provides for the transfer of a methylene or an ethylidene group to a variety of cyclic and acyclic olefins with the latter reagents having the advantage of being stable, crystalline materials. One of the problems associated with some of these reagents is the fact that a significant amount of the alkylidene moiety is lost to side reactions so that undesirably high ratios of reagents must be used. It seemed possible that sulfonium salts of other metals might also have potential as cyclopropanating agents and that a d^8 metal such as Ni(II) might provide some inherent stabilization to a carbenoid ligand in comparison to a d^6 metal such as Fe(II).

Experimental Section

Preparative work was conducted under a nitrogen atmosphere by using either a Vacuum Atmospheres glovebox or standard Schlenk glassware. Solvents were distilled under nitrogen from the appropriate drying agents before use. Ethylenebis(triphenylphosphine)nickel(0),[10] chlorocyclopentadienyl(triphenyl-

---

[1] O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869 and references cited.

[2] McBride, D. W.; Dudek, E.; Stone, F. G. A. *J. Chem. Soc.* **1964**, 1752.

[3] (a) Yoshida, G.; Kwosawa, H.; Okawara, R. *J. Organomet. Chem.* **1976**, *113*, 85, (b) *Ibid.* **1977**, *131*, 309.

[4] Taube, R.; Steinborn, D. J. *J. Organomet. Chem.* **1974**, *65*, C9.

[5] Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2699.

[6] Stein, J.; Facker, J. P.; Paparizos, C.; Chen, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 2192.

[7] Booth, B. L.; Smith, K. G. *J. Organomet. Chem.* **1981**, *220*, 219.

[8] Gregory, A. R.; Lindeman, J. A.; Mintz, E. A.; Tangvald, T.; Ward, A. S. 11th International Conference on Organometallic Chemistry, Pine Mountain, GA, 1983, Abstract #60.

[9] Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.

0276-7333/85/2304-1178$01.50/0

Table I. ^{1}H NMR Spectral Data

		chemical shifts, δ			
compound	solv	S–CH_3	S–CH_3	C_5H_5	other groups
$[Ni(PPh_3)(\eta^2\text{-}CH_2SCH_3)(Cl)]$	*a*	1.59	2.20		Ph, 7.5 (m)
$[Ni(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)]PF_6$	*a*	2.62 (m)	1.70		Ph, 7.4 (m)
	b	2.36	1.79		Ph, 7.37 (m)
$[Ni(\eta^5\text{-}(C_5H_5)(PPh_3)(\eta^1\text{-}CH_2SCH_3)]$	*c*	1.55 (d, $J_{P\text{-}H}$ = 7 Hz)	1.75	5.32	Ph, 7.42 (m)
$[Ni(\eta^5\text{-}C_5H_5)(PPhMe_2)(\eta^1\text{-}CH_2SCH_3)]$	*d*	1.62 (d, $J_{P\text{-}H}$ = 7 Hz)	2.00	5.17	Ph, 7.30 (m); Me 1.15 (d, $J_{P\text{-}H}$ = 10 Hz)
$[Ni(\eta^5\text{-}C_5H_5)[P(OMe)_3](\eta^1\text{-}CH_2SCH_3)]$	*c*	1.83 (d, $J_{P\text{-}H}$ = 7 Hz)	2.03	5.25	Me, 3.37 (d, $J_{P\text{-}H}$ = 11 Hz)
$[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2S(CH_3)_2]PF_6$	*d*	1.65 (d, $J_{P\text{-}H}$ = 8 Hz)	2.50	5.42	Ph, 7.8 (m)
$[Ni(\eta^5\text{-}C_5H_5)(PPhMe_2)CH_2S(CH_3)_2]PF_6$	*d*	*f*	2.77	5.43	Ph, 7.7 (m); Me, 1.77 (d, $J_{P\text{-}H}$ = 10 Hz)
$\{Ni(\eta^5\text{-}C_5H_5)[P(OMe)_3]CH_2S(CH_3)_2\}PF_6$	*d*	2.12 (d, $J_{P\text{-}H}$ = 7 Hz)	2.92	5.48	Me, 3.74 (d, $J_{P\text{-}H}$ = 12 Hz)
$\{Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6$	*d*	0.67 (t, $J_{P\text{-}H}$ = 10, $J_{H\text{-}H}$ = 10 Hz) 1.61 (dd, $J_{P\text{-}H}$ = 5, $J_{H\text{-}H}$ = 10 Hz)	1.96	5.18	Ph, 7.15 (m)
$[Ni(\eta^5\text{-}C_5H_5)(PPhMe_2)I]$	*e*			5.20	Ph, 7.65 (m), Me, 1.90 (d, $J_{P\text{-}H}$ = 11 Hz)
$[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2CN]$	*b*			5.17	Ph, 7.6 (m), CH_2, 0.07 (d, $J_{P\text{-}H}$ = 8 Hz)

[a] Methylene chloride. [b] Acetonitrile. [c] Benzene. [d] Acetone. [e] Chloroform. [f] Resonance obscured by phosphorus methyl resonance.

phosphine)nickel(II),[11] chloromethyl methyl sulfide,[12] trimethylsulfonium tetrafluoroborate,[13] (cyanomethyl)lithium[14] dimethylsulfonium methylide,[15] 2-lithio-1,3-dithiane,[16] and [(thiomethoxy)methyl]lithium[17] were synthesized or generated according to literature procedures. Methyl trifluoromethanesulfonate, iodomethane, and trimethyl phosphite (Aldrich Chemical Co.) and dimethylphenylphosphine (Strem Chemical Co.) were used as received. Methyl sulfide and tetramethylethylenediamine (Aldrich Chemical Co.) were distilled from CaH_2 before use. Solutions of *n*-butyllithium in hexane (Alfa Chemical Co.) were standardized by the method of Kofron and Baclawski.[18]

NMR spectra were obtained on Varian T-60 and Bruker A-2000 spectrometers with tetramethylsilane as an internal standard. Infrared spectra were recorded as Nujol mulls on a Beckman 4240 spectrophotometer.

NMR data for new compounds are given in Table I.

$[Ni(PPh_3)(\eta^2\text{-}CH_2SCH_3)Cl]$. A 2-g (3.3-mmol) sample of $[Ni(C_2H_4)(PPh_3)_2]$ was suspended in 20 mL of ether and, after being cooled to 0 °C, was treated dropwise with 0.32 g (3.3 mmol) of $ClCH_2SCH_3$. The mixture darkened considerably upon addition, and after 30 min an orange crystalline solid had formed. The mixture was allowed to warm to room temperature, and stirring was continued for 1.5 h after which the product was collected, washed with ether, and dried under vacuum; yield 1.15 g or 84%. Anal. Calcd for $C_{20}H_{20}NiPSCl$: C, 57.57; H, 4.79. Found: C, 56.39; H, 4.75. This complex was determined to be monomeric (found 440, calcd 417) in methylene chloride by an isopiestic molecular weight determination using 4-bromobiphenyl as standard.

$[Ni(PPh_3)_2(CH_2SCH_3)Cl]$. a. From $[Ni(C_2H_4)(PPh_3)_2]$. As described for the monophosphine complex in the previous preparation from 2 g of $[Ni(C_2H_4)(PPh_3)_2]$ except that the reaction mixture incorporated 1 equiv of triphenylphosphine and the dark red product was collected after the reaction mixture was warmed to room temperature; yield 2.19 g.

b. From $[Ni(PPh_3)_2Cl_2]$. A suspension of 1.96 g (3 mmol) of the dichloride complex was suspended in 10 mL of THF and, after being cooled to 0 °C, was treated with a solution of $LiCH_2SCH_3$ in hexane (1 equiv) over 1–2 min. Upon addition, an immediate color change from green to red occurred and a brick red crystalline solid began to form after about 15 min. After warming to room temperature, the mixture was stirred overnight after which the solid was collected and dried under vacuum; yield 1.15 g or 56%. Although all of the properties of these materials were consistent with their proposed formulations, satisfactory analytical data could not be obtained. Attempts to purify the materials by recrystallization were not successful.

$[Ni(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)]PF_6$. An acetone solution of $[Ni(PPh_3)_2(\eta^1\text{-}CH_2SCH_3)Cl]$, 1.0 g (1.47 mmol) in 20 mL, was treated with an acetone solution of 0.48 g (2.94 mmol) of NH_4PF_6. The dark solution lightened in color, and a small amount of white solid precipitated. After this precipitate was removed, the solution was concentrated under vacuum, which resulted in the formation of a yellow solid. This material was collected, washed with ether, and dried under vacuum; yield 0.91 g or 78% of analytically pure product. Anal. Calcd for $C_{38}H_{35}F_6NiP_3S$: C, 57.81; H, 4.44. Found: C, 57.30; H, 4.60.

$[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^1\text{-}CH_2SCH_3)]$. A suspension of 2.5 g (6 mmol) of $[Ni(PPh_3)(\eta^2\text{-}CH_2SCH_3)Cl]$ in 75 mL of THF was treated with 1.05 g (6 mmol) of NaC_5H_5·glyme, which resulted in the formation of a dark green solution. After the solution was stirred for 1 h, the THF was evaporated, the dark green residue was extracted with ether, and the extracts were filtered through Celite, taking care to wash the Celite pad with ether until the washings were nearly colorless. Evaporation of most of the ether and treatment of the residue with hexane gave a green solid that was collected, washed with a small amount of hexane, and dried under vacuum; yield 2.1 g or 77%.

b. From $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)Cl]$. A solution of 1.5 g (3.5 mmol) of the precursor complex in 40 mL of THF was cooled to −40 °C and rapidly treated with 1 equiv of $LiCH_2SCH_3$ in hexane. This caused an immediate change in color from dark red to green. The solution was allowed to slowly warm to room temperature over 1 h after which the solvent was removed under vacuum and the green residue extracted with ether. The ether extracts were treated as in part a to give the product; yield 1.1 g or 67%. Anal. Calcd for $C_{25}H_{25}NiPS$: C, 67.21; H, 5.60. Found: C, 66.72; H, 5.74.

$\{Ni(\eta^5\text{-}C_5H_5)(PPh_3)[CH_2S(CH_3)_2]\}O_3SCF_3$. A benzene solution containing 2.46 g (5.5 mmol) of $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^1\text{-}CH_2SCH_3)]$ was treated with 0.9 g (5.5 mmol) of $CH_3OSO_2CF_3$, which resulted in the immediate precipitation of a green crystalline solid. The green solid (3.3 g) was collected by filtration and was recrystallized from CH_2Cl_2/C_6H_6; 2.5 g was obtained in the first crop and 0.57 g in a second crop after evaporation of some of the solvent; total yield 3.07 g or 91%. Anal. Calcd for $C_{27}H_{28}F_3NiPO_3S_2$: C, 51.42; H, 4.61. Found: C, 51.49; H, 4.62.

$\{Ni(\eta^5\text{-}C_5H_5)(PPh_3)[CH_2S(CH_3)_2]\}PF_6$ and $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6$. Several variations were attempted but in general they involved treating a THF solution of $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)Cl]$, after being cooled to −78 °C, with a THF solution containing 1 equiv of dimethylsulfonium methylide, which was introduced by cannulation. The reaction mixture changed immediately from dark red to dark green. After the mixture was stirred for ca. 0.5 h at −78 °C, it was rapidly warmed to room temperature with a water bath, the volume of the solution was reduced, and any white precipitate was removed by filtration. Ether was added to the filtrate until cloudiness persisted, and the mixture was then cooled in an ice bath to induce crystallization. This material was metathesized to the hexaflurophosphate salt by dissolution in acetone with subsequent filtration followed by the addition of an aqueous solution of NH_4PF_6. The product was collected, washed with water, and dried under vacuum.

---

(10) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3019.
(11) Rausch, M. D.; Chang, Y. F.; Gordon, H. B. *Inorg. Chem.* **1969**, *8*, 1355.
(12) Bordwell, F. G.; Pitt, B. M. *J. Am. Chem. Soc.* **1955**, *77*, 572.
(13) Ohkubo, K.; Yamabe, T. *J. Org. Chem.* **1971**, *36*, 3149.
(14) Kaiser, E. M.; Hauser, C. R. *J. Org. Chem.* **1968**, *33*, 3402.
(15) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
(16) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231.
(17) Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717.
(18) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

Usually the product consisted of comparable amounts of the mono- and dinuclear complexes although on occasion one product would predominate. Fractional crystallization of the mixture from acetone/H_2O gave the dinuclear complex in pure form. It was much more difficult to obtain pure mononuclear complex from this mixture. Slow evaporation of an acetone solution of the dinuclear complex gave bright green crystals of the acetone solvate that were suitable for crystallography. Anal. Calcd for $C_{52}H_{53}F_6Ni_2OP_3S$: C, 59.46; H, 5.05. Found: C, 59.24; H, 5.11.

$\{Ni(\eta^5\text{-}C_5H_5)[PPh(CH_3)_2]I\}$. A solution of 1.0 g (3.3 mmol) of $[NiCp(CO)]_2$ in 20 mL of diethyl ether at −20 °C was treated with an ethereal solution of I_2 (3.3 mmol in 20 mL). The resulting black suspension was stirred for 30 min after which a benzene solution of $PPhMe_2$ (6.6 mmol in 40 mL) was added, and the reaction mixture was allowed to warm to room temperature and was then stirred for 14 h. After the solution was filtered, the solvent was removed under vacuum and the deep red-violet residue dissolved in 3:1 hexane/benzene and cooled to −20 °C. The red-violet solid that crystallized was collected while cold, washed with cold hexane, and dried under vacuum; yield 1.63 g or 64%. Anal. Calcd for $C_{13}H_{16}INiP$: C, 40.16; H, 4.16. Found: C, 40.40; H, 4.21.

$\{Ni(\eta^5\text{-}C_5H_5)[P(OCH_3)_3]I\}$. A solution of [NiCp(CO)I] was prepared as described in the previous preparation and was combined with 6.6 mmol of trimethyl phosphite dissolved in 40 mL of benzene and treated as for the $PPhMe_2$ complex except that the residue was dissolved in 9:1 hexane/benzene before being cooled to induce crystallization; yield of golden-brown product 1.6 g or 65%. This product was identical (^1H NMR spectrum) with material prepared in a similar manner by Werner.[19]

$\{Ni(\eta^5\text{-}C_5H_5)[PPh(CH_3)_2][CH_2S(CH_3)_2]\}PF_6$. A solution of 1.0 g (2.67 mmol) of $[Ni(\eta^5\text{-}C_5H_5)PPh(CH_3)_2I]$ in 25 mL of THF at −78 °C was treated with 1.1 equiv of $LiCH_2SCH_3$ in hexane. The resulting green solution was stirred for 1 h and then allowed to warm slowly to room temperature. After the solvent was removed under vacuum, the green residue was extracted with benzene and filtered through alumina (activity I). Evaporation of the filtrate yielded a dark green oil that would not crystallize but whose ^1H NMR spectrum was entirely consistent with that expected for $\{Ni(\eta^5\text{-}C_5H_5)[PPh(CH_3)_2](\eta^1\text{-}CH_2SCH_3)\}$. This material was dissolved in 1 mL of benzene and treated with excess methyl iodide which resulted in the precipitation of a green, oily solid. After the supernatant was decanted off, this material was dissolved in acetone and treated with an aqueous solution of NH_4PF_6 to yield a green microcrystalline solid that was collected, washed with water, and dried under vacuum; yield 0.35 g or 28%. Anal. Calcd for $C_{16}H_{24}F_6NiP_2S$: C, 39.78; H, 5.01. Found: C, 40.03; H, 5.02.

$\{Ni(\eta^5\text{-}C_5H_5)[P(OCH_3)_3][CH_2S(CH_3)_2]\}PF_6$. This preparation was performed exactly as described for the $PPhMe_2$ complex. The iodide salt was a green microcrystalline product; yield 0.62 g or 52%. This material was metathesized quantitatively to the hexafluorophosphate salt. Anal. Calcd for $C_{11}H_{22}F_6NiO_3P_2S$: C, 28.17; H, 4.73. Found: C, 28.48; H, 4.56.

General Procedure for Reactions of $\{Ni(\eta^5\text{-}C_5H_5)(L)[CH_2S(CH_3)_2]\}X$ with Nucleophiles. The salt was dissolved, along excess nucleophile in $Me_2SO\text{-}d_6$ and the reaction mixture monitored by ^1H NMR until the cyclopentadienyl resonance of the starting material had disappeared. In general, the reactions were very clean with the resonances due to the product being the only ones observed upon disappearance of the reactant. NMR spectra of independently prepared products were obtained for comparison. Some reactions were also conducted in a similar fashion in benzene with identical results.

$[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2CN)]$. A solution of $LiCH_2CN$ was generated at −78 °C by the addition of 0.15 g of acetonitrile in 3 mL of THF to a mixture of 3 mL of THF and 2.8 mL of a 1.33 M solution of butyllithium in hexane. After the mixture was stirred for 1 h, a THF solution of $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)Cl]$, 1.5 g (3.56 mmol) in 20 mL, was added over several minutes. The resulting dark green solution was stirred for 1 h at −78 °C and was then allowed to warm to room temperature. After the solvent was removed under vacuum, the residue was treated with ether and the mixture filtered through Celite. The dark green filtrate was concentrated under vacuum, which gave, after treatment with a small amount of hexane, a dark green crystalline product. The product was collected and dried under vacuum; yield 1.0 g or 66%. Anal. Calcd for $C_{25}H_{22}NNiP$: C, 70.49; H, 5.16; N, 3.29. Found: C, 70.11; H, 5.44; N, 3.24.

Table II. Crystal Data for $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6 \bullet C_3H_6O$

mol wt	1050.4
dimens, mm	*a*
space group	*Pbcm*
unit cell const[b]	
a, Å	11.20 (1)
b, Å	18.814 (6)
c, Å	24.40 (1)
no. of reflctns used to determine cell constants and their 2θ limits, deg	15 and $6.5 < 2\theta < 13.4$
Z	4
ρ_{calcd}, g cm^{-3}	1.357
ρ_{exptl}, g cm^{-3} [c]	1.35

[a] The crystal was lost before accurate measurements were taken; no dimension was smaller than 0.2 mm. [b] Data collected at 22 °C. [c] By flotation in carbon tetrachloride/hexane.

Table III. Data Collection and Refinement Details for $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6 \bullet C_3H_6O$

diffractometer	Syntex $P2_1$
monochromator (Bragg 2θ angle, deg)	graphite (12.2)
radiatn, Å	Mo K$\bar{\alpha}$, 0.710 69
takeoff angle, deg	6.75
scan method	θ–2θ
scan speed, min/max, deg min^{-1}	2.0/29.3
scan width, deg	2.0
bkgd/scan time ratio (TR)[a]	1.0
no. of stds (monitoring freq, no. of reflctns)	3[b] (97)
2θ limits of data, deg	$4 < 2\theta < 50$
k,k,l	$0,0,0 \rightarrow +h,+k,+l$
no. of data	4670
no. of data used in final refinement	2100[c]
no. of data/number of variable	7.6
μ,[d] cm^{-1}	8.8
$R = (\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/(\sum\lvert F_o\rvert)$ (function minimized = $\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2$)	0.11
R_w[e]	0.096

[a] Background counts measured before (BG1) and at the end (BG2) of the scan. Intensities determined from the total scan (CT) and background (BG) counts by I = CT − TR(BG1 + BG2). $\sigma_I = [CT + (TR)^2(BG1 + BG2)]^{1/2}$; $F_o = (I/Lp)^{1/2}$ where Lp is the Lorentz and polarization correction. [b] Standard reflections were 0,0,4; 0,3,0; 8,0,0. [c] $F > 3\sigma_F$. [d] No absorption correction was applied. [e] $R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)(w^{1/2})/[\sum(\lvert F_o\rvert)(w^{1/2})]$; $w = n/(\sigma_F^2 + mF^2)$. In the final cycle n was 2.44 and m was 1.57×10^{-3}.

General Procedure for Cyclopropanation of Cyclooctene by $[Ni(\eta^5\text{-}C_5H_5)(L)CH_2S(CH_3)_2]X$. The salt was dissolved (or suspended, depending on the choice of solvent) in a measured amount of solvent (1–2 mL) containing the required amount of cyclooctene. The resulting mixture (or solution) was heated at reflux for the duration of the reaction time. The flask was then cooled, and the volatiles were removed under high vacuum (<10^{-4} torr) or the nickel complexes were precipitated by addition of hexane. The yield of bicyclo[6.1.0]nonane was determined by gas chromatographic analysis using diphenylmethane as an internal standard. Gas chromatographic analysis of cyclopropanation reaction mixtures was done on a Varian Series 1400 chromatograph equipped with a thermal conductivity detector. Base-line separations were obtained with a 1.5% OV-101 (5 ft × 1/8 in.) on Chrom G column, using a column temperature program of 75–180 °C at 15 °C/min.

Structure Determination on $\{Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6 \cdot C_6H_6O$. Crystal data and details of data collection and refinement are given in Tables II and III. All computations were carried out on a CDC Cyber 730 computer using Sheldrick's SHELX-76 program package with minor local modifications. Scattering factors were taken from the usual source;

---

(19) Clemens, J.; Neukomm, H.; Werner, H. *Helv. Chim. Acta* **1974**, *22*, 516.

Table IV. Final Positional Parameters for Non-Hydrogen Atoms of $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6\bullet C_3H_6O$

atom	x	y	z
Ni	0.1227 (2)	0.12039 (9)	0.12109 (7)
P1	0.2631 (3)	0.0684 (2)	0.0771 (2)
P2	0.1039 (7)	0.4208 (4)	0.25000
S	0.1396 (5)	0.1337 (3)	0.25000
F1	−0.029 (2)	0.427 (1)	0.25000
F2	0.112 (2)	0.4775 (7)	0.2055 (6)
F3	0.229 (2)	0.413 (2)	0.25000
F4	0.088 (2)	0.3616 (7)	0.2938 (5)
C2	0.3789 (9)	0.1420 (5)	−0.0083 (4)
C3	0.3900 (9)	0.1652 (5)	−0.0624 (4)
C4	0.3062 (9)	0.1444 (5)	−0.1015 (4)
C5	0.2113 (9)	0.1004 (5)	−0.0866 (4)
C6	0.2002 (9)	0.0773 (5)	−0.0329 (4)
C1	0.2840 (9)	0.8981 (5)	0.0066 (4)
C8	0.3084 (8)	−0.0556 (6)	0.0297 (4)
C9	0.2913 (8)	−0.1387 (6)	0.0246 (4)
C10	0.2090 (8)	−0.1735 (6)	0.0582 (4)
C11	0.1437 (8)	−0.1350 (6)	0.0968 (4)
C12	0.1608 (8)	−0.0618 (6)	0.1019 (4)
C7	0.2431 (8)	−0.0271 (6)	0.0683 (4)
C14	0.4323 (9)	0.1490 (5)	0.1285 (5)
C15	0.5388 (9)	0.1626 (5)	0.1563 (5)
C16	0.6205 (9)	0.1078 (5)	0.1651 (5)
C17	0.5958 (9)	0.0394 (5)	0.1461 (5)
C18	0.4894 (9)	0.0258 (5)	0.1184 (5)
C13	0.4077 (9)	0.0806 (5)	0.1095 (5)
C19	0.010 (2)	0.155 (1)	0.0577 (7)
C20	−0.062 (2)	0.123 (1)	0.099 (1)
C21	−0.039 (2)	0.166 (2)	0.1452 (8)
C22	0.041 (2)	0.222 (1)	0.138 (1)
C23	0.068 (2)	0.215 (1)	0.078 (1)
C24	0.172 (1)	0.0782 (7)	0.1916 (5)
C25	0.263 (2)	0.199 (1)	0.25000
AC1[a]	0.577 (8)	0.387 (7)	0.25000
AC2	0.731 (6)	0.307 (4)	0.25000
AC3	0.653 (8)	0.349 (8)	0.25000
O	0.551 (6)	0.315 (3)	0.25000

[a] AC indicates a carbon atom in the acetone of solvation.

those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components using the dispersion factors given by Cromer. The structure was solved by standard heavy-atom techniques. All non-hydrogen atoms were located in successive difference Fourier maps and were subjected to full anisotropic treatment. Hydrogen atom positions were calculated, and only their thermal parameters were allowed to vary. Final positional parameters for non-hydrogen atoms are given in Table IV. Positional parameters for hydrogen atoms, thermal parameters for all atoms, and structure factor tables are given as supplementary material.

Results and Discussion

Reaction of $[NiCp(PPh_3)Cl]$ with $(CH_3)_2SCH_2$. At the onset of this work it appeared that the most direct route to $\{NiCp(L)[CH_2S(CH_3)_2]\}^+$ should be the direct reaction of $[NiCp(L)X]$ with preformed dimethylsulfonium methylide. In fact, treatment of $[NiCp(PPh_3)Cl]$ complex with the ylide in THF at −78 °C resulted in the instantaneous formation of the dark green color expected for such a complex. In one preparation a 52% yield of $\{NiCp(PPh_3)[CH_2S(CH_3)_2]\}^+$ was obtained (as the hexafluorophosphate salt). This product was reported earlier by Booth and co-workers;[7] however, their analytical results were not particularly good and their ^1H NMR data and melting point (176–180 °C vs. 155–157 °C for our product) are very different from those for our complex. Whereas Booth's compound exhibited singlets at δ 2.45 and 2.86 assigned to the methylene and methyl group resonances, respectively, our complex exhibited a doublet at δ 1.66 for the methylene group and a singlet at δ 2.53 for the methyl resonance. The similarity of these chemical shifts, and phosphorus coupling, to that observed for the dinuclear species $\{[NiCp(PPh_3)CH_2]_2SCH_3\}^+$ described below makes it very unlikely that the material prepared by Booth is the correct one.

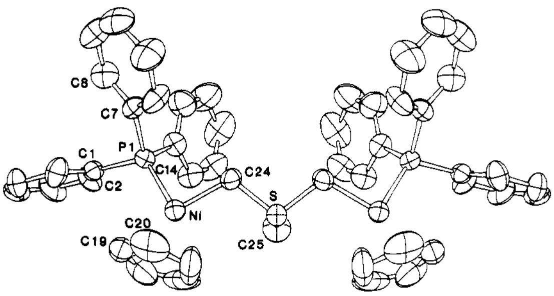


Figure 1. ORTEP drawing of the cation $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}^+$. Hydrogen atoms are not shown. Probability ellipsoids are at the 50% level.

In other preparations, and many were attempted, a second product was always obtained and in some cases it was the major one. This product resisted identification for some time but was finally shown to be a salt of the dinuclear cation $\{[NiCp(PPh_3)CH_2]_2SCH_3\}^+$ by a single-crystal X-ray structure (described in a following section). Subsequent reexamination of the ^1H NMR spectrum revealed resonances for the diastereotropic methylene protons that had been previously missed because of their complexity and low intensity. These resonances are a pseudotriplet at δ 0.67 ($J_{P\text{-}H}$ = 10 Hz, $J_{H\text{-}H}$ = 10 Hz) and a doublet of doublets at δ 1.61 ($J_{P\text{-}H}$ = 5 Hz, $J_{H\text{-}H}$ = 10 Hz). These assignments of coupling constants were confirmed by decoupling experiments. The above dinuclear product must be formed by the reaction sequence shown in eq 1 and 2. Note that the overall stoichiometry of the reaction

$$\{NiCp(PPh_3)[CH_2S(CH_3)_2]\}^+ + (CH_3)_2SCH_2 \rightarrow (CH_3)_3S^+ + \{NiCp(PPh_3)[CH_2S(CH_3)CH_2]\} \quad (1)$$

$$\{NiCp(PPh_3)[CH_2S(CH_3)CH_2]\} + [NiCp(PPh_3)Cl] \rightarrow \{[NiCp(PPh_3)CH_2]_2SCH_3\}^+ + Cl^- \quad (2)$$

is the same for formation of either the mononuclear or dinuclear product; the ratio of products formed must depend upon the relative rates of proton transfer between $\{NiCp(PPh_3)[CH_2S(CH_3)_2]\}^+$ and the ylide and the reaction of the ylide with the chloro complex. In spite of several attempts we were never able to successfully establish a reproducible procedure for the preparation of the mononuclear species as the major product. Since separation of the two salts was rather tedious, this method of preparation was abandoned as a source of the mononuclear complex and alternative routes were considered (vide infra).

Description of the Structure of $\{[NiCp(PPh_3)CH_2]_2SCH_3\}PF_6\cdot C_3H_6O$. The crystal structure of this complex consists of cations of the indicated formulation with noninteracting hexafluorophosphate anions and acetone molecules of crystallization. All three species have crystallographically imposed mirror symmetry. In the case of the cation the sulfur atom and methyl group carbon lie on the mirror plane; all three carbon atoms and the oxygen atom of the acetone molecule are on the mirror plane. Both the acetone molecule and the hexafluorophosphate ion were disordered and did not refine satisfactorily. A perspective drawing of the cation is shown in Figure 1, and a listing of selected interatomic angles and distances is given in Table V. The quality of the crystallographic data is such that a detailed analysis of the structural parameters is not warranted. However, it appears that the Ni–CH_2 distance is very similar to Ni–C(sp^3) distances determined for other $[Ni(Cp)(PPh_3)R]$ complexes (1.935 (6) and 1.952

Table V. Interatomic Distances (Å) and Angles (deg) in the Cation $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}^+$

Distances			
Ni–P1	2.141 (4)	Ni–C_{Cp}(av)	2.121 (17)
Ni–C24	1.972 (13)	P–C(av)	1.821 (12)
C24–S	1.804 (13)	C_{Cp}–C_{Cp}(av)	1.394 (27)
C25–S	1.846 (22)		
Angles			
C24–S–C25	103.6 (7)	C24–S–C24	104.5 (8)
C24–Ni–P1	92.8 (4)	S–C24–Ni	113.6 (7)

(6) Å in $[NiCpCH_2PPh_2]_2$;[20] 1.95 (3) Å in $[NiCpPPh_3CF_3]$[21]). The S–CH_2 and S–CH_3 distances of 1.804 (13) and 1.846 (22) Å, respectively, are similar to those reported by Helquist for $\{FeCp(CO)_2[CH_2SMe_2]\}$-$FSO_3$ (S–CH_2 = 1.784 (3) Å; S–CH_3 = 1.787 (3) Å).[1] This is the first structurally characterized complex containing the $[CH_3S(CH_2)_2]^-$ anion. The only other complex known to contain this ligand is also a dinuclear complex, $\{[ReCp(NO)(PPh_3)CH_2]_2SMe\}^+$. In this case the structure was proposed on the basis of the ^1H NMR spectrum.[22]

Preparation and Alkylation of $[NiCp(L)(CH_2SCH_3)]$. On the basis of Helquist's successful alkylation of $[FeCp(CO)_2(\eta^1\text{-}CH_2SCH_3)]$[1] and Sepelak's earlier alkylations of $\{NiCp(PPh_3)[\eta^1\text{-}CH_2N(CH_3)_2]\}$[23] and $\{FeCp(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$,[24] it seemed likely that $[NiCp(L)(\eta^1\text{-}CH_2SCH_3)]$ could be converted to sulfonium salts in a similar fashion. This route required the synthesis of the (thiomethoxy)methyl complexes which were unknown. $[NiCp(L)(\eta^1\text{-}CH_2SCH_3)]$ (L = PPh_3, $PPhMe_2$, $P(OMe)_3$) were prepared by reaction of [NiCp(L)Cl] with $LiCH_2SCH_3$ and for L = PPh_3 by the reaction sequence shown in eq 3 and 4. The oxidative addition route was

$$[Ni(C_2H_4)(PPh_3)_2] + ClCH_2SCH_3 \xrightarrow{\text{ether}} [Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)] \tag{3}$$

$$[Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)] + Cp^- \rightarrow [NiCp(PPh_3)(\eta^1\text{-}CH_2SCH_3)] + Cl^- \tag{4}$$

also of interest because the reactions of both Pd(0) and Pt(0) phosphine complexes with $ClCH_2SCH_3$ had already been studied.[3] Several attempts to conduct the reaction of $Ni(C_2H_4)(PPh_3)_2$ with $ClCH_2SCH_3$ in benzene, which was used as solvent for the Pd and Pt reactions, failed to give the desired product. However, the reaction was successfully conducted by addition of the chloromethyl methyl sulfide to a suspension of the ethylene complex in ether. These conditions were patterned after Uhlig's procedure[25] for oxidative addition of benzyl halides to Ni(0), a reaction that also does not work well in benzene. A crucial feature in both cases appears to be the insolubility of the product in ether.

If the above oxidative addition was conducted in the presence of an equivalent of triphenylphosphine, dark red $[Ni(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)]$ was obtained. This complex could also be obtained by reaction of $[Ni(PPh_3)_2Cl_2]$ with 1 equiv of $LiCH_2SCH_3$, but it was very difficult to separate the complex from the lithium chloride. Metathesis of the bis(phosphine) complex to $[Ni(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)]PF_6$ could be accomplished by using NH_4PF_6 in acetone. Treatment of $[Ni(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)]$ with THF or recrystallization from CH_2Cl_2/ether results in complete conversion to orange $[Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)]$. This complex, like its Pd analogue,[3] was determined to be monomeric in methylene chloride solution. The ^1H NMR spectrum of $[Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)]$ contained two singlets for the (thiomethoxy)methyl group. Similar observations were made for the corresponding palladium complex at room temperature although at −30 °C coupling of both the methyl and methylene hydrogens to phosphorus was observed.[3a] These results suggests that phosphine exchange must be occurring rapidly at the higher temperature. It should be noted that $[Pt(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)]$ does not spontaneously dissociate phosphine and the monophosphine complex, which was prepared by reaction with H_2O_2, does not contain an η^2-CH_2SCH_3 group but is a dinuclear species in which the sulfur atom of each thiomethyl group is coordinated to the other platinum atom such that a six-membered ring was formed.[3b] This is consistent with our earlier conclusion that an aminomethyl or allyl group was much more likely to be π bonded to nickel than to platinum.[26] The behavior of the (thiomethoxy)methyl complexes suggests that palladium is more like nickel than platinum in this connection.

Although $[Ni(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)]$ is a dark red solid, its methylene chloride solutions were identical in color with those of the η^2 complex. This suggests that 1 equiv of phosphine dissociates upon dissolution. This is supported by the fact that the ^1H NMR spectra of the two compounds were identical (except for the relative intensity of the phenyl to aliphatic resonances). Addition of several equivalents of triphenylphosphine to a methylene chloride solution of $[Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)]$ did result in some broadening of both the methyl and methylene proton resonances and a slight upfield shift of the latter, but there was no visible change in the color of the solution.

In ^1H spectra obtained on methylene chloride solutions of $\{Ni(PPh_3)_2[\eta^2\text{-}CH_2SCH_3]\}PF_6$, the methylene group protons were observed as two multiplets. This is consistent with η^2 bonding of the (thiomethoxy)methyl group and slow inversion of the asymmetric sulfur atom as was observed for the analogous Pd compound.[3a] However, in acetonitrile the methylene protons appeared to be equivalent. This is probably a result of an η^2 to η^1 interconversion for the (thiomethoxy)methyl group that is induced by coordination of acetonitrile.

Treatment of $[Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)]$ with sodium cyclopentadienide produced $[NiCp(PPh_3)CH_2SCH_3]$ in good yield. Although $[Ni(PPh_3)_2(Cl)(\eta^1\text{-}CH_2SCH_3)]$ could also be used for this reaction, the similarity in the solubility properties of the cyclopentadienyl complex and PPh_3 makes the monophosphine the preferred reagent.

The $PPhMe_2$ and $P(OMe)_3$ analogues of $[NiCp(PPh_3)CH_2SCH_3]$ were prepared by the reaction sequence shown eq 5–7. It was not possible to crystallize the (thiomethoxy)alkyl complexes with these ligands so that they were characterized in solution by their ^1H NMR spectra and by

$$[CpNiCO]_2 + I_2 \xrightarrow{-20\ ^\circ C} 2[CpNi(CO)I] \tag{5}$$

$$[CpNi(CO)I] + L \rightarrow [CpNi(L)I] \tag{6}$$

$$[CpNi(L)I] + LiCH_2SCH_3 \rightarrow [CpNi(L)(\eta^1\text{-}CH_2SCH_3)] \tag{7}$$

---

(20) Lindner, E.; Bouachir, F.; Hiller, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1146.

(21) Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1969**, 266.

(22) McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57.

(23) Sepelak, D. J.; Pierpont, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 6178.

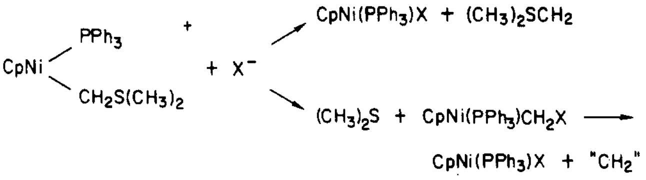
(24) Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6542.

(25) Hipler, B.; Uhlig, E.; Vogel, J. *J. Organomet. Chem.* **1981**, *218*, C1.

(26) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. G. *Organometallics* **1982**, *1*, 103.

conversion to the sulfonium salts with methyl iodide. It might be noted that other methods that have been successfully used for the preparation of $[CpNi(PPh_3)X]$[27] did not work for preparation of the $PPhMe_2$ or $P(OMe)_3$ derivative.

Scheme I



Alkylation of $[CpNi(L)(\eta^1\text{-}CH_2SCH_3]$ (L = $PPhMe_2$, $P(OMe)_3$) to give the sulfonium salts was accomplished by addition of methyl iodide to *concentrated* benzene solutions of the complexes. The iodide salts were converted to hexafluorophosphates by metathesis with NH_4PF_6 in acetone/water. Better yields were obtained for the triphenylphosphine complex when methyl triflate was used as the alkylating agent.

Reactions of $\{NiCp(L)[CH_2S(CH_3)_2]\}^+$ with Nucleophiles. When we initially attempted to alkylate $[CpNi(PPh_3)\eta^1\text{-}CH_2SCH_3]$ with methyl iodide in benzene none of the desired product was obtained. Instead, a homogeneous, dark red-purple solution formed from which $[NiCp(PPh_3)I]$ was isolated. It was subsequently found that if methyl iodide was added to concentrated solutions of the complex, at least moderate yields of the alkylation product could be obtained. Thus it seemed likely that $\{NiCp(L)[CH_2S(CH_3)_2]\}^+$ was reacting with iodide ion to produce the iodonickel complex. Peterson[28] observed a similar reaction in his attempts to alkylate $Sn(Bu)_3CH_2SCH_3$ with methyl iodide. In this case the only tin-containing product was $Sn(Bu)_3I$. Further investigations showed that $\{NiCp(L)[CH_2S(CH_3)_2]\}^+$ reacted essentially quantitatively with $[N(Bu)_4]Br$ in benzene to produce $[NiCp(PPh_3)Br]$. The formation of halonickel complexes by reaction with halide nucleophiles could occur by either of the pathways shown in Scheme I. The second pathway would require that the halomethyl complex be rather unstable as no evidence for an intermediate was observed. Evidence for the first pathway was obtained by examination of the reaction of $\{NiCp(PPh_3)[CH_2S(CH_3)_2]\}PF_6$ with $[(CH_3)_4N]CN$ in Me_2SO. $[NiCp(PPh_3)CN]$ was the exclusive product. There is little doubt that this product arises from displacement of $(CH_3)_2SCH_2$ since independently synthesized $[NiCp(PPh_3)(\eta^1\text{-}CH_2CN)]$ is a very stable compound. This previously unknown complex was prepared from the chloronickel complex and $LiCH_2CN$ and was characterized by analysis and infrared and NMR spectra. Similar reactivity toward CN^- was noted for the $P(OMe)_3$, but the $PPhMe_2$ complex was not investigated.

Reactions of $\{NiCp(L)[CH_2S(CH_3)_2]\}^+$ with Cyclooctene. $\{NiCp(PPh_3)[CH_2S(CH_3)_2]\}^+$ was surveyed for reactivity (cyclopropanation) toward cyclooctene under a variety of conditions as outlined in Table VI. The maximum yield of bicyclo[6.1.0]nonane obtained under any conditions was 49%. Under these conditions (refluxing acetonitrile, 2:1 olefin/complex ratio) the initially homogeneous reaction mixture rapidly deposited a black solid and ultimately became very dark in color. In other experiments it was determined that detectable decomposition of the nickelated sulfonium salt occurred after 90 min in refluxing acetonitrile in the absence of the cyclooctene. At 65 °C no cyclopropanation or visible decomposition occurred after 24 h. $\{FeCp(CO)_2[CH_2S(CH_3)_2]\}BF_4$ gave a 61% yield of the bicyclononane in refluxing acetonitrile (2:1 olefin/complex).

Table VI. Cyclopropanation of Cyclooctene by $[NiCp(L)CH_2S(CH_3)_2]^+$

L	solv	olefin/ complex	reactn time, h	yield, %
PPh_3[a]	THF	2:1	26	27
PPh_3[a]	dioxane	2:1	16	9
PPh_3[a]	CH_3CN	2:1	17	49
PPh_3[a]	CH_3CN	1:2	15	28
PPh_3[a]	CH_3CN	5:1	42	47
PPh_3[a]	cyclooctene		24	30
PMe_2Ph[b]	CH_3CN	2:1	24	19
$P(OMe)_3$[b]	CH_3CN	3:1	20	47
$P(OMe)_3$[b]	dioxane	2:1	20	25

[a] Triflate counterion. [b] Hexafluorophosphate counterion.

The activities of the $PPhMe_2$ and $P(OMe)_3$ complexes for cyclopropanation were also briefly surveyed. As indicated in the table, the yield of bicyclononane from the phosphite complex was comparable to that of the PPh_3 complex with the $PPhMe_2$ complex giving a somewhat lower yield.

The obvious conclusion to be made from these studies is that none of the three nickel complexes offers a better alternative to $\{FeCp(CO)_2[CH_2SMe_2]\}^+$ salts for cyclopropanation. Although the NiCp(L) moiety might be expected to stabilize a cationic methylene group relative to $FeCp(CO)_2$, there may be other modes of reaction for either the starting complex or a methylene intermediate that result in reduced cyclopropane formation. It would be especially interesting to determine the reactivity patterns of free alkylidenenickel complexes if they could be synthesized. Unfortunately, neither vinyl or α-alkoxyalkyl complexes of $[NiCpL]^{1+}$ are known so that the same methods used for synthesis of iron alkylidenes from similar precursors cannot be applied.[9,29-33] The possibility that carbenoid species might be obtained by hydride abstraction from alkyl complexes[34] is under consideration.

Registry No. $[Ni(PPh_3)(\eta^2\text{-}CH_2SCH_3)(Cl)]$, 96348-84-4; $[Ni(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)]PF_6$, 96348-86-6; $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^1\text{-}CH_2SCH_3)]$, 96348-87-7; $[Ni(\eta^5\text{-}C_5H_5)(PPhMe_2)(\eta^1\text{-}CH_2SCH_3)]$, 96348-88-8; $[Ni(\eta^5\text{-}C_5H_5)[P(OMe)_3](\eta^1\text{-}CH_2SCH_3)]$, 96348-89-9; $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2S(CH_3)_2]PF_6$, 80507-32-0; $[Ni(\eta^5\text{-}C_5H_5)(PPhMe_2)CH_2S(CH_3)_2]PF_6$, 96348-91-3; $[Ni(\eta^5\text{-}C_5H_5)[P(OMe)_3]CH_2S(CH_3)_2]PF_6$, 96348-93-5; $\{[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6$, 96348-95-7; $\{Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2]_2SCH_3\}PF_6{\cdot}C_3H_6O$, 96348-96-8; $[Ni(\eta^5\text{-}C_5H_5)(PPhMe_2)I]$, 55997-53-0; $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)CH_2CN]$, 96348-97-9; $[Ni(PPh_3)_2(CH_2SCH_3)Cl]$, 96348-98-0; $\{Ni(\eta^5\text{-}C_5H_5)(PPh_3)[CH_2S(CH_3)_2]\}O_3SCF_3$, 96348-99-1; $\{Ni(\eta^5\text{-}C_5H_5)[P(OCH_3)_3]I\}$, 55046-31-6; $\{Ni(\eta^5\text{-}C_5H_5)[PPh(CH_3)_2][CH_2S(CH_3)_2]\}I$, 96349-00-7; $\{Ni(\eta^5\text{-}C_5H_5)[P(OCH_3)_3][CH_2S(CH_3)_2]\}PF_6$, 96394-01-3; $[NiCp(PPhMe_2)Cl]$, 96349-01-8; $[NiCp(P(OMe)_3Cl]$, 43047-46-7; $[NiCp(PPh_3)I]$, 1298-82-4; $[NiCp(PPh_3)Br]$, 1298-79-9; $[Ni(C_2H_4)(PPh_3)_2]$, 23777-40-4; $[Ni(PPh_3)_2Cl_2]$, 14264-16-5; [Ni-

---

[27] Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. 1, p 450.

[28] Peterson, D. J. *J. Organomet. Chem.* **1971**, *26*, 215.

[29] Casey, C. P.; Miles, W. H.; Tudada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

[30] Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119.

[31] Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

[32] Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806.

[33] Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808.

[34] Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *Ibid.* **1983**, *105*, 4958 and references to other examples cited.

(η^5-C_5H_5)(PPh_3)Cl], 31904-79-7; [NiCp(CO)]$_2$, 12170-92-2; [NiCp(CO)I], 55046-35-0; [NiCp(PPh_3)CN], 42378-02-9; $ClCH_2SCH_3$, 2373-51-5; $LiCH_2SCH_3$, 286-60-2; CH_3I, 74-88-4; $LiCH_2CN$, 20428-58-4; dimethylsulfonium methylide, 6814-64-8; cyclooctene, 931-88-4; bicyclo[6.1.0]nonane, 286-60-2.

Supplementary Material Available: Tables of thermal parameters for non-hydrogen atoms, positional and thermal parameters of hydrogen atoms, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Reactivity of Bridging Phosphido Ligands in WOs Binuclear Complexes. Crystal and Molecular Structure of $(CO)_5W(\mu$-$PPh_2)Os(H)(CO)_2(PMePh_2)(PPh_2H)$

Steven Rosenberg and Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Arnold L. Rheingold

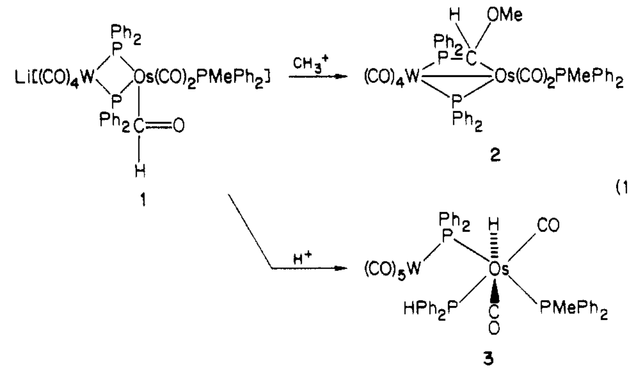
Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received October 26, 1984

The binuclear complex $(CO)_5W(\mu$-$PPh_2)Os(H)(CO)_2(PMePh_2)(PPh_2H)$, **3**, is obtained from protonation of the formyl compound $Li[(CO)_4W(\mu$-$PPh_2)_2Os(CHO)(CO)_2(PMePh_2)]$. Complex **3** has been characterized by a complete single-crystal X-ray diffraction study. It crystallizes in the space group $C2/c$ with a = 35.172 (9) Å, b = 11.045 (3) Å, c = 25.275 (6) Å, β = 105.89 (2)°, V = 9444 (3) Å^3, and Z = 8. The structure has been refined for the 5365 reflections with $F_o \geq 3\sigma(F_o)$ to R_F = 0.036 and R_{wF} = 0.041. The two nonbonded metal atoms are bridged by the μ-PPh_2 ligand with the W further coordinated by five CO's and the Os by two CO's, the hydride, PPh_2H, and $PMePh_2$ ligands. Both the Os hydride and the hydrogen on phosphorus were located and refined. The W–P_μ–Os angle of 116.2 (1)° is the largest yet reported for this structural unit and illustrates the tremendous flexibility of this bridging ligand. Thermolysis of **3** leads to CO and H_2 loss with formation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2O}s(CO)_2(PMePh_2)$, **4**, which involves formation of a second phosphido bridge. A second phosphido bridge also forms upon reaction of **3** with MeLi to give $Li[(CO)_4W(\mu$-$PPh_2)_2Os(H)(CO)_2(PMePh_2)]$, **5**, after loss of CO. If MeI is added immediately after addition of MeLi, the product is instead the monophosphido-bridged complex $(CO)_5W(\mu$-$PPh_2)Os(H)(CO)_2(PMePh_2)_2$, **6**, formed as a mixture of two isomers. Protonation of **5** leads to the bridge cleavage product $(CO)_5\overline{W\text{-}(\mu\text{-}PPh_2)O}s(H)(CO)(PMePh_2)(PPh_2H)$, **7**, while methylation with $[(CH_3)_3O]BF_4$ leads to formation of **4**. Complex **4** is also obtained when solutions of **7** are heated to 55 °C.

Bridging phosphido ligands have recently been shown to participate in a number of interesting chemical transformations.[1-16] These include conversion of bridging phosphido ligands into bridging phosphinidene,[6,8] phosphine oxide,[9] and diphosphene ligands[10] and coupling of bridging phosphido ligands with alkyl,[1,3] alkyne,[11,16] vinyl,[12] hydride,[1,13] carbene,[1,2,14] and phosphide ligands.[14] An understanding of the types of reactions that these ligands undergo and the conditions under which they occur will be necessary for polynuclear reactivity and catalytic studies of phosphido-bridged complexes.

We recently reported that methylation and protonation of the phosphido-bridged WOs formyl complex **1** led to the phosphido rearrangements given in eq 1.[1,2] Particularly



(1)

interesting was complex **2** which apparently arose via coupling of a phosphido ligand with a carbene, the latter generated by methylation of the formyl ligand. Protonation of **1** led cleanly to complex **3** in which one μ-PPh_2 ligand had been converted into a terminal PPh_2H ligand. We have since investigated the derivative chemistry of **3**

---

(1) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519.

(2) Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934.

(3) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782.

(4) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846.

(5) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.

(6) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251.

(7) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L. *Inorg. Chem.* **1984**, *23*, 1779.

(8) Patel, V. D.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 99.

(9) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

(10) Vahrenkamp, H.; Wolters, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 154.

(11) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 814.

(12) Henrick, K.; Iggo, J. A.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1984**, 209.

(13) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826.

(14) Yu, Y.-F.; Chau, C.-N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.* **1984**, *106*, 3704.

(15) Shyu, S.-G.; Wojcicki, A. *Organometallics* **1984**, *3*, 809.

(16) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

0276-7333/85/2304-1184$01.50/0