ORGANOMETALLICS

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Organometallics, **1983**, 2 (12), 1901-1903• DOI: 10.1021/om50006a043 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Stannocenes and 2 exhibit a similar chemical behavior toward HBF_4, which cleaves the molecules. Analogous to the formation of cation[8] $[(C_5Me_5)Sn]^+$ we obtain a cationic dinuclear species. The constitution of the brown solid

$$2 + HBF_4 \rightarrow [(C_5H_5)Co(C_2B_2C)Sn]^+BF_4^- + 1$$

follows from analytical and ^1H NMR data.[13] It exhibits a large high-field shift for the proton of the 1,3-diborolenyl ring in comparison to that of 2. An excess of HBF_4 destroys the sandwich 1.

Acknowledgment. This research was supported by generous grants from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft.

Registry No. 2, 87711-03-3.

Supplementary Material Available: Tables of positional and thermal parameters and structure factors and details of the structure analysis (49 pages). Ordering information is given on any current masthead page.

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[13] ^1H NMR (THF-d_8, Me_4Si): δ 4.41 (s, 5), 2.3 (m, 2), 1.8 (m, overlap with THF-d_8), 1.08 (tr, 6), 0.90 (s, 6), 0.05 (s, 1).

Possibilities of 1,1-Dimethylsilole as a Ligand in Transition-Metal Chemistry

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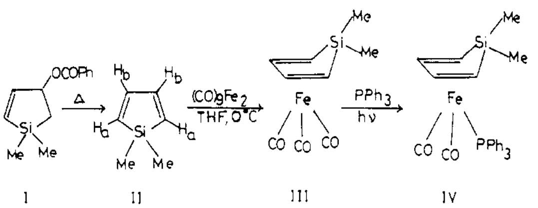
Summary: 1,1-Dimethylsilole is an effective ligand for transition-metal complexes. Direct displacement of carbonyl ligands from $Fe_2(CO)_9$ and $Co_2(CO)_8$ results in the stable complexes $(\eta^4\text{-}C_4H_4SiMe_2)Fe(CO)_3$ and $[(\eta^4\text{-}C_4H_4SiMe_2)(CO)_2Co]_2$, respectively. $(\eta^4\text{-}C_4H_4SiMe_2)(CO)_3Fe$ undergoes carbonyl replacement with PPh_3. Cleavage of the cobalt-cobalt bond is achieved with both iodine and sodium amalgam. The anion obtained from the reduction with sodium amalgam displaces chloride in Ph_3SnCl. Displacement of 1,5-cyclooctadiene in $(1,5\text{-COD})_2Ni$ and $(1,5\text{-COD})Mo(CO)_4$ affords the Ni^0 sandwich complex $(\eta^4\text{-}C_4H_4SiMe_2)_2Ni$ and the molybdenum complex $(\eta^4\text{-}C_4H_4SiMe_2)_2Mo(CO)_2$, respectively.

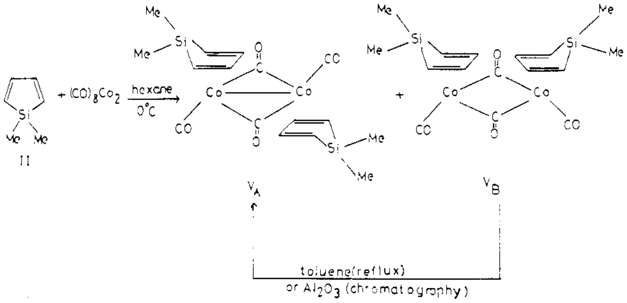
Transition-metal complexes of substituted siloles are well-known[1] and are interesting as potential sources of the unknown (η^5-silacyclopentadienyl)metal complexes.

Recently two groups reported the synthesis of 1,1-dimethylsilole[2,3] from the readily available 3,3-dimethyl-3-silacyclopentene, thus potentially allowing access into C-unsubstituted silole–transition-metal complexes. The recent report by Dubac and co-workers on the trapping of 1,1-dimethylsilole with iron carbonyl[4] prompts us to report our results concerning the complexation of 1,1-dimethylsilole with iron, cobalt, molybdenum, and nickel.

Scheme I



Scheme II



1,1-Dimethylsilole (prepared from the benzoate ester I[3] was collected in THF at −196 °C. After being warmed to 0 °C, the solution was transferred to a flask containing an excess (twice the equimolar amount) of $Fe_2(CO)_9$ and stirred at 0 °C for 40 min. After this time the solution was warmed to room temperature and allowed to stir for 2 h. Removal of the solvent afforded an oil that was chromatographed on silica gel with hexane. The yellow band was collected and concentrated to afford a yellow oil that was shown by ^1H NMR to be the silole complex III and the dimer of dimethylsilole[3] in 90:10 ratio. Pure III[5] was obtained by elution with hexane through a short silica gel column containing 10% $AgNO_3$ (52% yield based on I) (Scheme I).

UV irradiation of III with an equimolar amount of Ph_3P in hexane resulted in the substitution of a carbonyl ligand. The complex IV was obtained as yellow-orange crystals after chromatography on silica gel with hexane and crystallization (42% yield)[6] (Scheme I).

In an analogous synthesis of III, an excess of 1,1-dimethylsilole was reacted with $Co_2(CO)_8$ at 0 °C using hexane as the solvent. Careful crystallizations from hexane at −78 °C afforded an orange solid that was shown by ^1H NMR spectroscopy to be a mixture of the two isomers V_A and V_B (32% yield based on $Co_2(CO)_8$)[7] (Scheme II). This is surprising since in the case of the reaction of 1,1-di-

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[1] Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2484 and references therein.

[2] Laporterie, A.; Mazerolles, P.; Dubac, J.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *206*, C25; **1981**, *216*, 321.

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[5] III: orange yellow oil; ^1H NMR (δ relative to $(CH_3)_4Si$ in CCl_4) 5.89 (m, H_b), 1.96 (m, H_a), 0.83 (s, endo-CH_3), −0.18 (s, exo-CH_3); IR (cyclohexane) ν (CO) 2055 (s), 1985 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 250 (molecular peak).

[6] IV: orange crystals; mp 170.5–171.5 °C; ^1H NMR (in C_6D_6, δ) 7.63–6.73 (m, aromatic), 5.00 (m, H_b), 1.17 (m, H_a), 0.70 (s, endo-CH_3), −0.14 (s, exo-CH_3); IR (cyclohexane) ν (CO) 1975 (s), 1920 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 484 (molecular peak). Anal. Calcd for $C_{26}H_{25}FeO_2PSi$: C, 64.46; H, 5.17; P. 6.40. Found: C, 64.61; H, 5.35; P. 6.53.

[7] V (mixture of isomers A and B): ^1H NMR (in C_6D_6, δ) 5.48 (m, H_b), 5.18 (m, H_b), 2.71 (m, H_a), 0.51 (s, endo-CH_3), 0.45 (s, endo-CH_3), −0.22 (s, exo-CH_3), −0.41 (s, exo-CH_3). Isomer V_A: red-orange crystals; mp 161–161.5 °C; ^1H NMR (C_6D_6, δ) 5.18 (m, H_b), 2.71 (m, H_a), 0.51 (s, endo-CH_3), −0.22 (s, exo-CH_3); IR (cyclohexane) ν(CO) 2020 (s), 2000 (s), 1830 (m) cm^{-1}; mass spectrum, *m/e* (assignment)) 450 (molecular peak). Anal. Calcd for $C_{16}H_{20}Co_2O_4Si_2$: C, 42.67; H, 4.44. Found: C, 42.52; H, 4.40.

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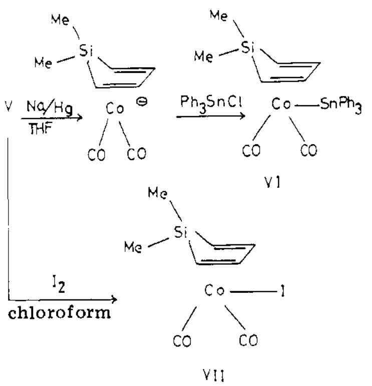
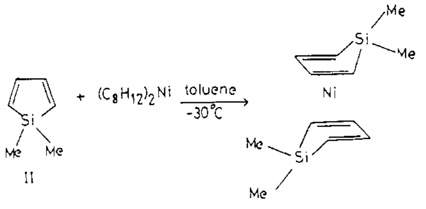
Scheme III



Scheme IV



methyl-2,5-diphenylsilole with $Co_2(CO)_8$ only one isomer was obtained (trans).[1] Pure V_A was obtained either by isomerization of V_B to V_A by heating a mixture of the two isomers for 3–4 h at 80 °C in toluene or by chromatography in either acid-washed or neutral alumina.

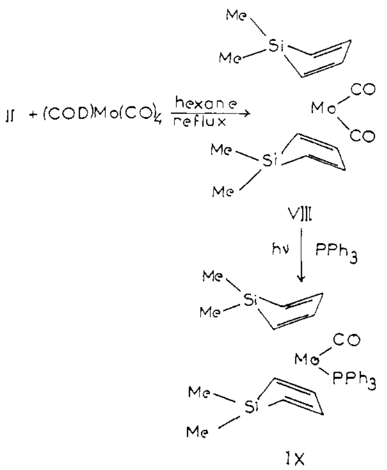
Complex V is isostructural with $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$ since both possess bridging carbonyls. Polarographic measurements (with a dropping mercury electrode, platinum wire as the anode, and a calomel-saturated electrode as the reference) showed one wave at −1.46 V. This reduction potential is to be compared to that of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$, −1.49 V, and of $Co_2(CO)_8$, −0.3 V.[8]

Reduction of complex V with a sodium amalgam[9] followed by reaction with Ph_3SnCl affords VI[10] as yellow crystals after chromatography on acid-washed alumina (hexane/ether (1/1)) and crystallization from hexane (Scheme III).

Treatment of complex V with a chloroform solution of iodine gave, after crystallization, red-violet crystals of VII[11] (52% yield) (Scheme III). The behavior of complex V differs from many other $[(\eta^4\text{-diene})(CO)_2Co]_2$ complexes in which the halogen derivatives are not isolable and decompose to $Co_4(CO)_2$.[12] This set of reactions shows the great stability of silole–cobalt complexes compared to that of the parent conjugated diene complexes. The silole ring behaves here as an η^5-cyclopentadienyl.

The bis(η^4-dimethylsilacyclopentadiene)nickel complex was obtained by adding 1,1-dimethylsilole to a suspension of $(1,5\text{-COD})_2Ni$[13] in toluene at −40 °C. The yellow suspension became an orange solution from which an orange oil was obtained. This oil was shown by ^1H NMR and mass spectroscopy to be the bis(silole) complex in an impure state[14] (Scheme IV). Attempts at purification by column chromatography led to its decomposition.

Scheme V



The displacement of a 1,5-COD ligand from a transition metal by the monomeric silole appears to be a general method of entry into other silole–transition-metal complexes. Hence, when a hexane solution of 1,1-dimethylsilole is added to a refluxing hexane solution of $(1,5\text{-COD})Mo(CO)_4$ followed by chromatography on Florisil with hexane the $(\eta^4\text{-silole})_2Mo(CO)_2$ complex VIII is obtained in 43% yield.[15] Irradiation of VIII with Ph_3P in benzene through a Pyrex filter (450-W external Hanovia lamp) results in the displacement of a CO to afford IX (81%, based upon reacted VIII)[16] (Scheme V). The comparison of the ^1H NMR spectra of complexes VIII and IX shows for the former two planes of symmetry since protons H_A (or H_B) are not distinguishable. One of these planes remains in the latter since protons H_A (or H_B) are nonequivalent. However, methyl protons (exo and endo) are identical for the two silole rings. This suggests that both silicon atoms are in the same symmetry plane. These structures are under investigation.

Dimethylsilole appears to be a good ligand for transition metals since it is not displaced by phosphines[17] (displacement of a carbonyl takes place instead) and since it behaves as a cyclopentadienyl ligand in the cobalt complex which is isoelectronic and isostructural with $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2]_2$.

Few η^4-conjugated diene complexes of cobalt and nickel are known[12,18] and their reactivity seems to be markedly different than for dimethylsilole complexes. Further studies are in progress.

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(10) VI: yellow crystals; mp 85.5–86.5 °C; ^1H NMR (C_6D_6, δ) 7.73 and 7.17 (m, aromatic), 5.18 (m, H_b), 2.72 (m, H_a), 0.47 (s, endo-CH_3), −0.36 (s, exo-CH_3); IR (cyclohexane) ν(CO) 2030 (s), 1980 (s) cm^{-1}; mass spectrum, *m/e* (assignment for ^{120}Sn) 576 (molecular peak). Anal. Calcd for $C_{26}H_{25}CoO_2SiSn$: C, 54.29; H, 4.35. Found: C, 54.34; H, 4.42.

(11) VII: violet crystals; mp 69.5–71 °C; ^1H NMR (δ) 5.97 (m, H_b), 2.40 (m, H_a), 0.40 (s, endo-CH_3), −0.36 (s, exo-CH_3); IR (cyclohexane) ν(CO) 2070 (s), 2040 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 352 (molecular peak). Anal. Calcd for $C_8H_{10}CoIO_2Si$: C, 27.29; H, 2.86. Found: C, 26.78; H, 3.01.

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(14) Orange red oil: ^1H NMR (C_6D_6, δ) 4.93 (m, H_b), 3.56 (m, H_a), 0.26 (s, endo-CH_3), 0.00 (s, exo-CH_3); mass spectrum, *m/e* (assignment for ^{58}Ni) 278 (molecular peak).

(15) VIII: yellow crystals; mp 61–62 °C; ^1H NMR (C_6D_6, δ) 4.84 (m, 4 H), 1.83 (m, 4 H), 0.40 (s, 6 H), −0.08 (s, 6 H); IR (hexane) ν(CO) 1990 (s), 1940 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 374 (molecular peak with ^{98}Mo). Anal. Calcd for $C_{14}H_{20}MoO_2Si_2$: C, 45.15; H, 5.37. Found: C, 45.15; H, 5.49.

(16) IX: yellow crystals; mp 193–194.5 °C; ^1H NMR (C_6D_6, δ) 6.90–7.70 (m, 15 H), 5.20 (m, 2 H), 4.40 (m, 2 H), 2.00 (m, 2 H), 1.50 (m, 2 H), 0.65 (s, 6 H), 0.10 (s, 6 H); IR (cyclohexane) ν(CO) 1890 (s), 1916 (s) cm^{-1}; mass spectrum, *m/e* (assignment) 608 (molecular peak with ^{98}Mo), 580 (loss of CO), 346 (loss of Ph_3P). Anal. Calcd for $C_{31}H_{35}MoOPSi_2$: C, 61.37; H, 5.82. Found: C, 61.50; H, 5.70.

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Registry No. I, 79005-20-2; II, 18135-88-1; III, 85944-69-0; IV, 87640-58-2; V_A, 87640-59-3; V_B, 87680-14-6; VI, 87640-60-6; VII, 87640-61-7; VIII, 87640-62-8; IX, 87640-63-9; $(CO)_9Fe_2$, 15321-51-4; $(CO)_8Co_2$, 10210-68-1; $(C_8H_{12})_2Ni$, 1295-35-8; (COD)$Mo(CO)_4$, 12109-74-9; nickel bis(dimethylsilole), 87640-64-0; dimethylsilole dimer, 78484-34-1.

Synthesis and Structure of a Bimetallic Diphosphenium Ion Complex Containing a Diazadiphosphetidine Ring

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Received August 30, 1983

Summary: The reaction of $\mathrm{NaMo}[\eta^5\text{-}(CH_3)_5C_5](CO)_3$ with $\mathrm{Cl\overline{PN(\mathit{t}\text{-}Bu)P(Cl)N}(\mathit{t}\text{-}Bu)}$ in a 2:1 ratio in THF results in the formation of a metallophosphenium ion complex $\mathrm{Mo_2[(CH_3)_5C_5]_2(CO)_4[\overline{PN(\mathit{t}\text{-}Bu)PN}(\mathit{t}\text{-}Bu)]}$. The compound has been characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and the structure has been determined by X-ray diffraction techniques. The neutral molecular complex can be considered to be derived from the union of the phosphorus atoms on a formal dicationic diazadiphosphetidine ring $[\mathrm{\overline{PN(\mathit{t}\text{-}Bu)PN}(\mathit{t}\text{-}Bu)^{2+}}]$ with the Mo atoms from two $\mathrm{Mo}[\eta^5\text{-}(CH_3)_5C_5](CO)_2^-$ fragments.

Heterolytic cleavage of phosphorus–halogen bonds in selected uncoordinated and metal-coordinated aminohalophosphines is promoted with classical halide acceptors and metal carbonylate nucleophiles. By utilizing this procedure, dicoordinate aminophosphenium ions[1] $[(R_2N)(X)P^+]$, cationic metallophosphenium ion complexes[2] $M(CO)_x[(R_2N)(X)P]^+$, and neutral metallophosphenium ion complexes[3] $M(CO)_y[(R_2N)(X)P]$ have recently been prepared. The majority of the compounds have been obtained from monophosphine ligands, and only a few attempts to prepare phosphenium ions from diphosphine precursors have been described. In particular, Scherer[4] observed that the combination of $AlCl_3$ and the diazadiphosphetidine $\mathrm{CH_3\overline{PN(\mathit{t}\text{-}Bu)P(Cl)N}(\mathit{t}\text{-}Bu)}$ results in the formation of a monophosphenium ion $\mathrm{CH_3\overline{PN(\mathit{t}\text{-}Bu)PN}(\mathit{t}\text{-}Bu)^+}$ (1), while Keat[5] noted the formation of a related monocation $[\mathrm{Me_2N\overline{PN(\mathit{t}\text{-}Bu)PN}(\mathit{t}\text{-}Bu)^+}]$ (2). Cowley and co-workers[1h] have investigated similar chemistry of 2,4-dichloro-1,3-di-*tert*-butyldiazadiphosphetidine, and even in the presence of excess $AlCl_3$ only the monocation $[\mathrm{Cl\overline{PN(\mathit{t}\text{-}Bu)PN}(\mathit{t}\text{-}Bu)^+}]$ (3) was found. No evidence for the formation of a dication $[\mathrm{\overline{PN(\mathit{t}\text{-}Bu)PN}(\mathit{t}\text{-}Bu)^{2+}}]$ (4) was reported. Diazadiphosphetidine ligands should provide a convenient template for the construction of a number of unusual metallophosphenium ion complexes,[6] and the rich chemistry of $\mathrm{X\overline{PN(\mathit{t}\text{-}Bu)P(X)N}(\mathit{t}\text{-}Bu)}$ ligands with metal carbonylate reagents have been examined in our laboratory.[7] We report here the synthesis and molecular structure determination for the first bimetallic diphosphenium ion complex that can be considered to contain the dication **4**.

Combination of $\mathrm{Cl\overline{PN(\mathit{t}\text{-}Bu)P(Cl)N}(\mathit{t}\text{-}Bu)}$[8] (**5**) with 2 equiv of $\mathrm{NaMo}[\eta^5\text{-}(CH_3)_5C_5](CO)_3$[9] in tetrahydrofuran (THF) results in the evolution of 90% of 2 equiv of CO, precipitation of NaCl, and the formation of a red-orange air-sensitive solid, **6**.[10,11] These observations and the spectroscopic and structural data described below are consistent with eq 1.

The infrared spectrum of **6** in cyclohexane shows two strong carbonyl bands at 2014 and 1931 cm^{-1} which is consistent with the presence of two terminal carbonyls on each molybdenum atom. The positions of these bands are similar to those reported for $\mathrm{Mo[(CH_3)_5C_5](CO)_2NO}$ (2015 and 1935 cm^{-1})[12] and higher in frequency than the bands found in $\mathrm{Mo[(CH_3)_5C_5](CO)_2[\overline{PN(CH_3)CH_2CH_2N}CH_3]}$ (1902 and 1810 cm^{-1}).[13] This suggests that the diphosphenium ion **4** displays π-acceptor ability similar to

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(10) Compound **6** was isolated under inert-atmosphere conditions. The THF solution was filtered, and the filtrate was vacuum evaporated. The resulting solid was extracted with benzene and recovered in 85% yield by vacuum evaporation of the benzene. Carbon monoxide was recovered in 90% yield from the original reaction mixture by using a Toepler pump: infrared spectrum (carbonyl region, cyclohexane) 2014 (s), 1931 cm^{-1}; ^{1}H NMR (benzene, Me_4Si standard) δ 1.65 (m, *t*-Bu methyl), 2.24 (s, Cp* methyl); ^{13}C{^{1}H} NMR (Me_4Si standard) δ 103.25 (s, Cp* ring), 31.59 (m, *t*-Bu methyl) 11.37 (d, $^3J_{CP} = 2.5$ Hz Cp* methyl); ^{31}P{^{1}H} NMR (85% H_3PO_4 standard) δ 224.65 (s).

(11) The monometallic complexes $\mathrm{Mo(CO)_2[\eta^5\text{-}(CH_3)_5C_5]\overline{PN(\mathit{t}\text{-}Bu)\text{-}P(Cl)N}(*\text{-}Bu)}$ and $\mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)\overline{PN(\mathit{t}\text{-}Bu)P(Cl)N}(\mathit{t}\text{-}Bu)}$ have also been prepared and fully characterized. These complexes will be described in full along with **4** in a future paper: Dubois, D. A.; Light, R. W.; Duesler, E. N.; Paine, R. T., to be submitted for publication.

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0276-7333/83/2302-1903$01.50/0