

addition, it is interesting to note that the isomerization of 1 to 2 proceeds via a least-motion path of  $C_s$  symmetry, as shown in Figure 1, while the parent silanone isomerizes via an out-of-plane path of  $C_1$  symmetry.<sup>2a-c</sup>

As Table I shows, the barrier for the 1,2-silyl shift in 1 to 2 is 30.7 kcal/mol at the HF/6-31G\* level. Addition of a set of p-type polarization functions on hydrogens (i.e., HF/6-31G\*\*//6-31G\*) has no effect on the barrier height. On the other hand, the inclusion of a set of diffuse sp function<sup>7</sup> and double sets of d-type polarization functions<sup>8</sup> on heavy atoms (i.e., HF/6-31+G(2d,p)//6-31G\*) lowers the HF/6-31G\* barrier only by 1.3 kcal/mol. These suggest that at the HF level the further extension of the basis set has no significant effect on the barrier height.

Thus, the effect of electron correlation was incorporated by means of Møller-Plesset (MP) perturbation theory up to full fourth-order (MP4SDTQ)<sup>9</sup> in the core-frozen approximation. As Table I shows, the MP calculations drop the HF barriers by ca. 6 kcal/mol: this dropping is rather insensitive to the order of perturbation. The most reliable energies at the MP4SDTQ/6-31+G(2d,p)//6-31G\* level yield a barrier of 22.9 kcal/mol for the 1,2-silyl shift in 1 to 2. Zero-point correction (ZPC) made with the HF/6-31G\* harmonic vibrational frequencies yields a final prediction of 22.7 kcal/mol for the classical barrier.

The predicted barrier is drastically small compared with that of 61 kcal/mol for the 1,2-H shift in the parent silanone. It appears that the relatively small barrier of 22.7 kcal/mol is readily surmountable at 610 °C where Barton and co-worker carried out their experiment:<sup>4</sup> conventional transition-state theory allows us to estimate the rate constant on the order of  $7.2 \times 10^5 \text{ s}^{-1}$  ( $\Delta H^\ddagger = 20.8 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -8.3 \text{ eu}$ )<sup>10</sup> at the temperature. On the other hand, the reverse reaction  $2 \rightarrow 1$  is unlikely to proceed under mild conditions, as is apparent from Table I. In fact, no experimental evidence for the isomerization of siloxy-silylene to silylsilanone has been found.<sup>4</sup>

The relatively small barrier for the 1,2-silyl shift is probably ascribable to the hypervalent ability of the shifting silicon at the transition state.<sup>11</sup> At this point, it is instructive that the barrier for the 1,2-SiF<sub>3</sub> shift in (SiF<sub>3</sub>)HSi=O to HSi—OSiF<sub>3</sub> was calculated to be 18.4 kcal/mol at the MP4SDTQ/6-31G\*\*//6-31G\* level and is 6.1 kcal/mol lower at the same level than that for the 1,2-SiH<sub>3</sub> shift. This lowering corresponds to the fact<sup>12</sup> that very electronegative substituents like F enhance the hypervalent bonding. In addition, it is important to note that the silicon atom in the SiF<sub>3</sub> group is more positively charged and thereby can interact more strongly with the negatively charged oxygen atom to be attacked.

In summary, we hope that the present calculations help obtain the definite experimental evidence for the interconversion of a silanone and a silylene.<sup>13</sup> The further

details of this work together with some other 1,2-shifts will be published in due course.

**Acknowledgment.** All calculations were carried out at the Computer Center for the Institute for Molecular Science, by using the GAUSSIAN 82 program<sup>14</sup> in the library program package.

(13) We have recently found that in the triplet state the 1,2-silyl shift proceeds without a significant barrier.

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### Oxidative Syntheses of Cyclopentadienyl $\eta^2$ -Acyl Complexes and Stereospecific Conversion to an $\eta^2$ -Ylide Complex. X-ray Crystal Structures of Cp(NO)(I)Mo( $\eta^2$ -C(O)-*p*-tol) and Cp(NO)(I)Mo( $\eta^2$ -C(O)(PMe<sub>3</sub>)-*p*-tol)

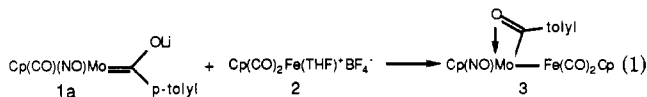
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Received February 12, 1987

**Summary:** Reaction of either Cp(NO)Mo( $\eta^2$ -C(O)-*p*-tol)-Fe(CO)<sub>2</sub>Cp (**3**) (*p*-tol = *p*-tolyl) or Cp(CO)(NO)Mo=C(OLi)R (**1**) with I<sub>2</sub> gives the  $\eta^2$ -acyl complexes Cp(NO)(I)Mo( $\eta^2$ -C(O)R) (**4**) (R = *p*-tol, 4-*t*-BuC<sub>6</sub>H<sub>4</sub>, Me). Oxidation of **4** (R = aryl) gives carboxylato complex **5**, while reaction of **4** (R = *p*-tol) with PMe<sub>3</sub> gives at least a 95:5 ratio of diastereomers of the ylide complex Cp(NO)(I)Mo( $\eta^2$ -C(O)(PMe<sub>3</sub>)-*p*-tol) (**6**).

The chemistry of transition-metal acyl complexes commands interest on the basis of their role in CO insertion reactions<sup>1</sup> and more recently in serving as templates for highly diastereoselective enolate reactions.<sup>2</sup> We recently reported the synthesis of two isomeric heterodinuclear  $\mu$ -acyl compounds, *cis*- and *trans*-Cp(CO)Fe( $\mu$ -C(O)-*p*-tol)( $\mu$ -CO)Mo(NO)Cp, formed via reaction of Cp(CO)(NO)Mo=C(OLi)R (**1a**, R = *p*-tol) and Cp(CO)<sub>2</sub>Fe(THF)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (**2**). During the course of this reaction we isolated a thermally unstable dinuclear intermediate and on the basis of spectroscopic data proposed the novel structure **3** shown in eq 1.<sup>3</sup> In order to obtain additional



chemical evidence for this structure, we attempted to oxidatively cleave the proposed metal-metal bond with iodine to give Cp(CO)<sub>2</sub>FeI and a perhaps more tractable molybdenum acyl complex. We report here (1) the successful

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(10) The thermodynamic quantities were evaluated with the statistical treatment, using the MP4SDTQ/6-31+G(2d,p)//6-31G\* energies and the HF/6-31G\* geometries and frequencies.

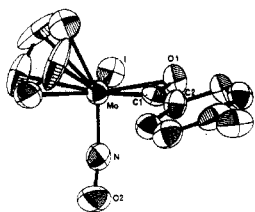
(11) For the mobility of silyl groups in silene and disilene, see: Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1392; *Organometallics* **1984**, *3*, 1320. Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H.; Schaefer, H. F.; Morokuma, K., Eds.; D. Reidel Publishing: Dordrecht, 1986; pp 249-267.

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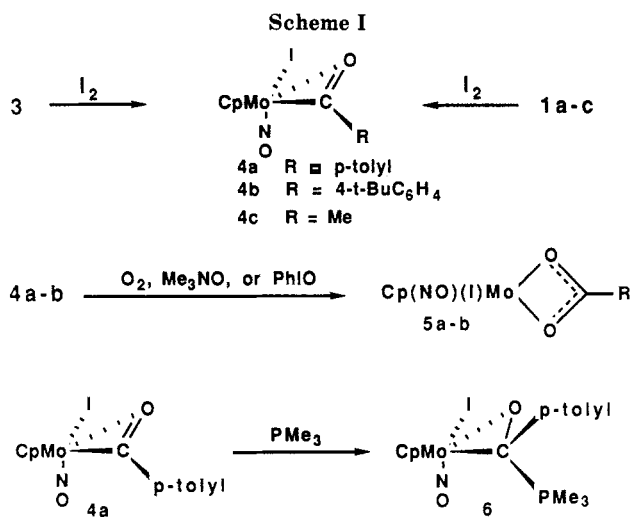
(1) See for instance: (a) Casey, C. P.; Baltusis, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6347-6353. (b) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *Ibid.* **1986**, *108*, 345-347.

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**Figure 1.** ORTEP drawing of **4a**. Selected bond distances (Å) and angles (deg): Mo–C(1), 2.065 (11); Mo–O(1), 2.228 (9); C(1)–O(1), 1.250 (13); C(1)–C(2), 1.422 (16); Mo–I, 2.770 (2); Mo–N, 1.796 (13); Mo–C(1)–O(1), 80.36 (70); Mo–O(1)–C(1), 66.06 (65); Mo–C(1)–C(2), 153.08 (94); O(1)–C(1)–C(2), 126.52 (113); Mo–N–O(2), 170.43 (124).



outcome of this reaction, involving formation of an  $\eta^2$ -acyl complex, (2) an alternative and apparently general synthesis of such  $\eta^2$ -acyls, (3) oxidation of the acyl to a carboxylato ligand, and (4) stereospecific conversion of the  $\eta^2$ -acyl complex to a rare  $\eta^2$ -phosphorus ylide complex.

Reaction of **3** with 1 equiv of I<sub>2</sub> in 20:1 ether/CH<sub>2</sub>Cl<sub>2</sub> at –78 °C for 0.5 h followed by warming to –10 °C for 1 h gave well-known Cp(CO)<sub>2</sub>FeI and a new molybdenum acyl complex (**4a**) in 79% and 56% isolated yields, respectively, based on the mononuclear starting materials **1a** and **2** (Scheme I). The spectroscopic data for **4a** were consistent with the simple iodide-substitution product shown; in particular, **4a** exhibited a terminal nitrosyl band in the IR at 1650 cm<sup>–1</sup>, an acyl carbonyl resonance at 253.3 ppm in the <sup>13</sup>C NMR, and a Cp resonance at  $\delta$  6.21 in the <sup>1</sup>H NMR. The acyl resonance is typical of both  $\eta^2$ - and  $\eta^1$ -acyls.<sup>2c,5</sup> The Cp resonance, however, is at unusually low

field. Since dimeric [Cp(NO)(I)Mo]<sub>2</sub>( $\mu$ -I)<sub>2</sub> exhibits similar NO and Cp bands,<sup>6</sup> an alternative structure for **4a**, [Cp(NO)( $\eta^1$ -C(O)-*p*-tolyl)Mo]<sub>2</sub>( $\mu$ -I)<sub>2</sub>, was also a reasonable possibility. An X-ray diffraction study<sup>7</sup> confirmed the mononuclear  $\eta^2$ -acyl structure shown (Figure 1). The bond lengths relating to the acyl ligand are comparable to those in related compounds<sup>2c,5b,8</sup> and require no comment. The one striking feature is the orientation of the  $\eta^2$ -acyl, which lies in a plane roughly parallel to the Mo–I bond and perpendicular to the Mo–NO axis: the angles between the Mo–C–O plane and the Mo–I and Mo–N axes are 6.9° and 75.5°, respectively. Furthermore, there is no spectroscopic evidence for rotation of this ligand,<sup>5b</sup> so the orientation with the oxygen atom next to the iodine atom may also be fixed. These stereochemical features are identical with those seen in Cp(NO)(PPh<sub>3</sub>)Re( $\eta^2$ -CH<sub>2</sub>O)<sup>+</sup>, in which extended Hückel MO calculations reproduce the observed orientation.<sup>9</sup> In both cases, the NO ligand presumably is the unique feature that controls the conformational preference, although in the Re (d<sup>6</sup>) case, this is due to an interaction between the d-orbital HOMO and the formaldehyde  $\pi^*$  LUMO, while in the Mo (d<sup>4</sup>) case it would involve donation from the oxygen sp<sup>2</sup> lone pair into the metal-centered LUMO.<sup>10</sup>

The knowledge that **4a** was a stable compound suggested that it might be prepared directly from **1**, without the intermediate use of **2** to give **3**. In fact, oxidation of the anionic acyls **1a–c** with iodine gave **4a–c** in 49–99% yield (Scheme I).<sup>11</sup> The method is apparently general, but since these compounds do not survive chromatography, difficulty in purification may limit its utility. This is a particular problem in the purification of **4c**, since its separation from [Cp(NO)(I)Mo]<sub>2</sub>( $\mu$ -I)<sub>2</sub>,<sup>6</sup> which is both the major byproduct in the synthesis of **4c** as well as its only observable thermal decomposition product,<sup>12</sup> can only be accomplished by tedious and yield-consuming recrystallizations. The aromatic acyls **4a,b** are not noticeably thermally sensitive. All three acyls undergo immediate air oxidation, but while no tractable products can be identified from the oxidation of **4c**, clean formation of carboxylato<sup>13</sup> derivatives **5a,b** was

(6) (a) King, R. B. *Inorg. Chem.* **1967**, *6*, 30–34. (b) Identification was based on comparison to an authentic sample: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  6.39. Bonnesen, P. V., unpublished results.

(7) **4a**: *P*2<sub>1</sub>/*a*, *T* = 26 °C, *a* = 13.766 (8) Å, *b* = 7.718 (4) Å, *c* = 14.227 (9) Å,  $\beta$  = 105.474 (15)°, *Z* = 4, *R* = 0.054. **6**: *P*2<sub>1</sub>/*a*, *T* = –140 °C, *a* = 12.225 (3) Å, *b* = 11.790 (3) Å, *c* = 13.467 (4) Å,  $\beta$  = 106.370 (5)°, *Z* = 4, *R* = 0.035. Full details of the solutions are available in the supplementary material.

(8) (a) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46–C48. (b) Guzman, E. C.; Wilkinson, G.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 229–234. (c) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360–6368. (d) Desmond, T.; Lalor, F. J.; Ferguson, G.; Ruhl, B.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 55–56. (e) Kreisl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem.* **1984**, *96*, 618–619. (f) Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214–3222. (g) Tilley, T. D. *Ibid.* **1985**, *107*, 4084–4085. (h) Jeffery, J. C.; Lawrence-Smith, J. G. *J. Chem. Soc., Chem. Commun.* **1986**, 17–19.

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(11) We find it necessary to isolate **1a–c** (formed most cleanly by reaction of CpMo(CO)<sub>2</sub>(NO) and RLi in ether at room temperature for R = aryl and in THF at –78 °C for R = Me) in order to obtain high yields of **4**. Treatment of **1a,b** with I<sub>2</sub> in ether at –10 °C for 15 min gave **4a,b** in 93–99% yield after CH<sub>2</sub>Cl<sub>2</sub> or CICH<sub>2</sub>CH<sub>2</sub>Cl extraction, while **4c** was best obtained (in 49% yield) by reaction in THF. Crystallization of **4a,b** was carried out in acetone/ether and crystallization of **4c** in CH<sub>2</sub>Cl<sub>2</sub>/hexane, at –35 °C.

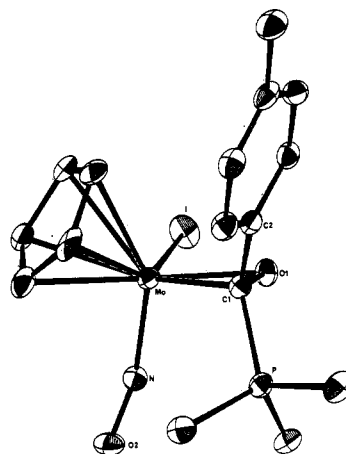
(12) Thermal decomposition is complete over the course of 1 week in acetone solution at room temperature; the fate of the acetyl ligand is unknown.

(4) **4a**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 1650 (m), 1582 (w) cm<sup>–1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.18 (d, *J* = 8.2 Hz), 7.63 (d, *J* = 8.0 Hz) (AA'BB', 4 H), 6.21 (s, 5 H, Cp), 2.56 (s, 3 H, Me); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>)  $\delta$  253.3 (acyl CO), 150.8 (C<sub>4</sub>), 134.0 (2 C), 131.4 (2 C), 127.4 (C<sub>1</sub>) (aromatic), 103.0 (Cp), 22.2 (Me); MS (EI, 70 eV), *m/e* 439 (M<sup>+</sup> for <sup>98</sup>Mo), 409 (M<sup>+</sup> – NO), 119 (*p*-tol-CO<sup>+</sup>); mp 150–157 °C dec. **5a**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 1677 (m), 1521 (mw), 1443 (m) cm<sup>–1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.90 (d, *J* = 8.3 Hz), 7.37 (d, *J* = 8.0 Hz) (AA'BB', 4 H), 6.49 (s, 5 H, Cp), 2.42 (s, 3 H, Me); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>)  $\delta$  185.8 (*p*-tol-CO<sub>2</sub>), 146.5 (C<sub>4</sub>), 130.2 (2 C), 129.5 (2 C), 128.1 (C<sub>1</sub>) (aromatic), 109.3 (Cp), 21.7 (Me); MS (EI, 70 eV), *m/e* 455 (M<sup>+</sup> for <sup>98</sup>Mo), 425 (M<sup>+</sup> – NO), 135 (*p*-tol-CO<sub>2</sub><sup>+</sup>), 119 (*p*-tol-CO<sup>+</sup>). **6**: IR (CHCl<sub>3</sub>) 1572 (vs) cm<sup>–1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.51 (d, *J* = 8.0 Hz), 7.27 (d, *J* = 8.0 Hz), 7.20 (d, *J* = 7.9 Hz), 7.15 (d, *J* = 7.8 Hz) (1 H each), 5.38 (s, 5 H, Cp), 2.33 (s, 3 H, Me), 1.82 (d, *J* = 13.3 Hz, 9 H, PMe<sub>3</sub>); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>)  $\delta$  143.4 (C<sub>1</sub>, d, *J* = 26.4 Hz), 136.6 (C<sub>4</sub>, d, *J* = 2.8 Hz), 130.4 (d, *J* = 1 Hz), 129.7 (d, *J* = 2.4 Hz), 126.0 (s), 124.3 (d, *J* = 4.3 Hz) (aromatic), 104.1 (Cp), 72.2 (d, *J* = 60.3 Hz, ylide CO), 20.9 (Me), 10.2 (d, *J* = 52.4 Hz, PMe<sub>3</sub>); MS (EI, 16 eV) same as **4a**, with *m/e* 76 (PMe<sub>3</sub><sup>+</sup>, base peak); mp 124–130 °C dec. Complete data for new compounds is available in the supplementary material.

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observed in the reactions of **4a,b**. Oxidation of **4a** with anhydrous  $\text{Me}_3\text{NO}$  or  $\text{PhIO}$  also gave **5a**, but less cleanly (Scheme I). Spectral<sup>14</sup> characterization<sup>14</sup> of **5a,b** was based on their mass spectra, in which the complex Mo isotope envelope of each of the precursor acyls is shifted by 16 amu to higher mass and by the replacement of the precursor acyl carbonyl resonance in the <sup>13</sup>C NMR by one typical of a carboxylate, near 186 ppm. Chemical evidence was provided by protonation of **5a** with  $\text{HBF}_4$  in  $\text{CDCl}_3$ , which yielded some *p*-toluic acid; **4a** is stable under these conditions. Lastly, in order to confirm the mononuclear structure, rather than a symmetrical iodide or carboxylato-bridged structure, oxidation of a mixture of **4a** and **4b** was carried out to give a mixture that by <sup>1</sup>H NMR contained only **5a** and **5b** and no signals that would have indicated a mixed *p*-tolyl/4-*t*-BuC<sub>6</sub>H<sub>4</sub> dimer.

In order to test the strength of the oxygen coordination to molybdenum in **4a**, we next combined it with CO and  $\text{PMe}_3$  in attempts to generate an  $\eta^1$ -acyl complex. No reaction of **4a** in acetone-*d*<sub>6</sub> under 12 atm of CO was observed at room temperature, while warming to 65 °C surprisingly yielded  $\text{CpMo}(\text{CO})_2\text{NO}$  and *p*-toluic acid. However, reaction with  $\text{PMe}_3$  occurred immediately at room temperature to generate ylide complex **6** (Scheme I). Key data<sup>4</sup> included a downfield signal at 30.8 ppm in the <sup>31</sup>P NMR and  $J_{\text{PH}}$  and  $J_{\text{PC}}$  values of 13.3 and 52.4 Hz, respectively, for the ylide  $\text{PMe}_3$  fragment, while the use of <sup>13</sup>CO-enriched  $\text{CpMo}(\text{CO})_2\text{NO}$  allowed the positive identification of the ylide carbon resonance in the <sup>13</sup>C NMR at 72.2 ppm.<sup>15</sup> Monitoring the  $\text{PMe}_3$  reaction by <sup>31</sup>P and <sup>1</sup>H NMR at 240 K gave evidence for formation of a second diastereomer, as judged by the observation of peaks in a 95:5 ratio at 31.8 and 29.9 ppm in the <sup>31</sup>P NMR and  $\delta$  5.36 and 5.97 in the <sup>1</sup>H NMR. However, the only evidence that the minor isomer—which irreversibly disappears upon warming to room temperature—is in fact the diastereomeric ylide is the unusually high-field <sup>31</sup>P NMR chemical shift. An X-ray diffraction study<sup>7</sup> of **6** revealed  $\text{PMe}_3$  coordinated to the acyl carbonyl on the side of the NO ligand, rather than that of the bulkier Cp ligand, with the orientation of the C–O portion of the ylide with respect to the Mo–I and Mo–N axes remaining virtually identical with that seen in **4a** (Figure 2). While the  $\eta^2$ -ylide structure was confirmed, the ligand in **6** also may be described as the  $\eta^2$ -acylphosphonium ion  $\text{Me}_3\text{PC}(\text{O})\text{-}p\text{-tol}^+$ . The geometry is remarkably similar to  $\eta^2$ -carbonyl complexes,<sup>9,16</sup> with respect to (1) the carbon–oxygen bond



**Figure 2.** ORTEP drawing of **6**. Selected bond distances (Å) and angles (deg): Mo–C(1), 2.171 (5); Mo–O(1), 2.078 (3); C(1)–O(1), 1.367 (6); C(1)–C(2), 1.505 (7); C(1)–P, 1.831 (5); Mo–I, 2.819 (1); Mo–N, 1.765 (4); Mo–C(1)–O(1), 67.58 (25); Mo–O(1)–C(1), 74.96 (25); Mo–C(1)–C(2), 119.70 (34); Mo–C(1)–P, 114.12 (24); O(1)–C(1)–C(2), 116.34 (41); O(1)–C(1)–P, 112.55 (34); C(2)–C(1)–P, 116.98 (35); Mo–N–O(2), 165.39 (38).

length, (2) the shorter Mo–O than Mo–C bond length, and (3) the attenuated pyramidalization about the carbonyl carbon.<sup>17</sup> Free acylphosphonium cations are well-known,<sup>18</sup> but to our knowledge **6** is the first simple coordination complex of this species to be described.<sup>19</sup> This formalism also has the interesting feature that the metal fragment, anionic  $\text{CpMo}(\text{I})\text{NO}^-$ , is now  $d^6$  and therefore isoelectronic with the orientationally similar rhenium formaldehyde complex described above.<sup>9</sup>

In conclusion, we have developed a simple and potentially general oxidative synthesis of new cyclopentadienyl  $\eta^2$ -acyl complexes, which are related to the well-known hydridotris(pyrazolyl)borate (Tp) molybdenum  $\eta^2$ -acyls.<sup>2c,5b</sup> The further oxidation of the Cp  $\eta^2$ -acyls to carboxylato complexes **5a,b** bears an interesting resemblance to the insertion of sulfur into the Mo–C bonds of  $\text{CpMo}(\text{NO})\text{R}_2$ <sup>20</sup> and the oxidation of  $\text{CpMo}(\text{CO})_3^-$  to give a carbonate ligand,<sup>21</sup> but it is nonetheless unusual in that only a single oxygen atom is incorporated. While reaction of phosphines with the related Tp complexes gives rise to CO substitution<sup>5b</sup> rather than ylide formation, this latter reaction channel has been observed in formally electron-deficient tantalum  $\eta^2$ -acyls.<sup>15g,17</sup> The most remarkable aspect of the formation of **6** is the high stereospecificity. Stereospecific reactions of related enolates are proposed to depend on steric interactions with neighboring phosphine groups,<sup>2,22</sup> yet here high stereospecificity is apparently mediated simply by a Cp ligand. Of course, the new stereocenter is adjacent to the chiral metal center here rather than one

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atom removed as in the enolate systems. Further work on the reactions and associated stereochemistry of these acyls is in progress.

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**Supplementary Material Available:** Spectroscopic data for new compounds, structure determinations for 4a and 6, ORTEP drawing and crystal packing diagrams for 4a and 6, and tables of crystal data, bond distances and angles, anisotropic temperature factors, and isotropic temperature factors for 4a and 6 (21 pages); listings of structure factor amplitudes for 4a and 6 (20 pages). Ordering information is given on any current masthead page.

### Formation of Si-Si Bonds from Si-H Bonds in the Presence of Hydrosilation Catalysts

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**Summary:** Complexes of Pt, Pd, Rh, and Ir that are known to catalyze the hydrosilation of alkenes are found to also catalyze the formation of Si-Si bonds from Si-H bonds. The relative rates of hydrosilation and Si-Si bond formation are measured for several catalysts.

The reactivity of Si-H bonds with transition metals is well-established and is frequently exploited to produce Si-C and Si-O bonds via hydrosilation of alkenes and carbonyl compounds, respectively,<sup>1</sup> and as a general synthetic method to produce organometallic complexes containing Si-M bonds.<sup>2</sup> There are, however, few examples of Si-Si bond formation in the presence of transition metals.<sup>3</sup> In fact, the only general method for the synthesis of Si-Si bonds is the Wurtz-type coupling of halosilanes in the presence of alkali metal,<sup>4</sup> in spite of the difficulties frequently encountered in using the method<sup>5</sup> and the currently widespread interest in using polysilanes as precursors to ceramic materials, as photoinitiators for vinyl-free radical polymerization and as photoresist materials.<sup>6</sup> Therefore, the observation in our laboratory of

**Table I. Reaction of R<sub>3</sub>SiH in the Presence of L<sub>2</sub>Pt(C<sub>2</sub>H<sub>4</sub>) (1)**

experiment <sup>a</sup>	silane	R <sub>3</sub> Si-SiR <sub>3</sub> , <sup>b</sup> %	others (% yield) <sup>b</sup>
1	PhMeSiH <sub>2</sub>	27	Ph <sub>2</sub> MeSiH (52)
2	PhMe <sub>2</sub> SiH	0 <sup>c</sup>	Ph <sub>2</sub> Me <sub>2</sub> Si (4)
3	Et <sub>3</sub> SiH	0 <sup>c</sup>	
4	Et <sub>2</sub> SiH <sub>2</sub>	95	
5	(EtO) <sub>3</sub> SiH	0 <sup>c</sup>	(EtO) <sub>4</sub> Si (61)
6	Et <sub>2</sub> SiH <sub>2</sub> + Et <sub>3</sub> SiH	Et <sub>4</sub> Si <sub>2</sub> H <sub>2</sub> , 58% Et <sub>5</sub> Si <sub>2</sub> H, 8%	

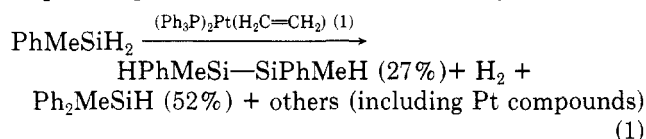
<sup>a</sup> 0.03 mmol of 1, 9 mmol of R<sub>3</sub>SiH. See footnote 8 for experimental details. <sup>b</sup> Yield as percentage of total products at 75-h reaction time. Products such as trimers, siloxanes (formed from traces of water), other disproportionation products, and unidentified compounds are not included in the table. <sup>c</sup> No reaction within our limits of detection (approximately 0.1%).

**Table II. Relative Rates of Disilane Formation and Hydrosilation in the Presence of Various Catalysts**

catalyst	A. Si-Si bond formation <sup>a</sup>	B. hydrosilation <sup>b</sup>
(Ph <sub>3</sub> P) <sub>2</sub> Pt(C <sub>2</sub> H <sub>4</sub> ) (1)	1.0 <sup>c</sup>	0.8
H <sub>2</sub> PtCl <sub>6</sub>	0.1	6
(PPh <sub>3</sub> ) <sub>2</sub> PtCl <sub>2</sub>	0.1	0.1
Pt(COD)Cl <sub>2</sub> (4)	0.7	70
(Ph <sub>3</sub> P) <sub>3</sub> RhCl (2)	31	400
[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (6)	5	60
(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Rh(C <sub>2</sub> H <sub>4</sub> )	0.2	0.7
RhCl <sub>3</sub>	0.3	3
[Rh(COD)Cl] <sub>2</sub>	1	25
[Ir(COD)Cl] <sub>2</sub> (5)	0.2	3
[Pd(allyl)Cl] <sub>2</sub> (3)	12	100

<sup>a</sup> 0.01 mmol of catalyst and 1.0 mmol of Et<sub>2</sub>SiH<sub>2</sub>. Rate values for disilane formation were obtained from the amount of time necessary to form 0.01 mmol of product. See text for further discussion of kinetics and footnote 9 for experimental details. <sup>b</sup> 0.01 mmol of catalyst, 1.0 mmol of Et<sub>2</sub>SiH<sub>2</sub>, and 1.0 mmol of 1-hexene. Values were obtained from the relative amounts of HEt<sub>2</sub>Si(*n*-hexyl)/disilane formed for each catalyst, corrected for detector response factors, and multiplied by the relative rate in column A. <sup>c</sup> This rate was arbitrarily assigned a value of 1, and all others are expressed relative to it.

formation of disilane HPhMeSi-SiPhMeH from PhMeSiH<sub>2</sub> in the presence of small amounts of (PPh<sub>3</sub>)<sub>2</sub>Pt-(H<sub>2</sub>C=CH<sub>2</sub>) (1)<sup>7</sup> warranted further investigation (eq 1).



The reactions of various silanes with catalytic amounts of 1 were examined first (Table I).<sup>8</sup> When the silane is

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