resonances of all of the proton and proton-bearing carbon atoms.[6]

The NOE difference experiments were especially informative, as irradiation of the resonance of H(4A) resulted in enhancement of the intensity of the resonance of H(10B); since these two H atoms are at opposite ends of the organic ligand, the result suggests a structure in which the diallylic ligand wraps around the metal atom. This conclusion was supported by molecular mechanics (MMX[7]) calculations and subsequently confirmed by X-ray crystallographic analysis.[8]

The structure of I (Figure 1) contains two mutually cis carbonyl groups, the C(1)–Fe–C(2) bond angle being 92.0 (2)°. The hydrocarbon framework is coordinated to the iron via the two η^3-allyl groups C(3)–C(5) and C(8)–C(10), involving the former TMM and isoprene constituents, respectively. The Fe–C(4) bond is marginally longer than the other iron–allyl bonds, but all are typical of (η^3-allyl)iron compounds in general.[9] Interestingly, I is much more thermally stable than is $Fe(CO)_2(\eta^3\text{-allyl})_2$,[10] which is reported to reductively eliminate diallyl at above room temperature. Presumably the ethylene backbone joining the two η^3-allylic fragments prevents intramolecular rearrangement to the orientation necessary for coupling and decoordination, although an oscillatory motion involving rotation about the C(6)–C(7) bond and comcomitant mutual reorientation of the two η^3-allyl–iron linkages seems likely since the resonances of H(6A,B) and H(7A,B) exhibit temperature-dependent chemical shifts.

The formation of I presumably involves initial coordination of the unsubstituted end of the isoprene, since trimethylamine oxide is required for the reaction to occur. Details of the subsequent coupling step are not obvious, but we note several apparently similar, photochemically induced coupling reactions of C_2F_4 to coordinated TMM[3] and η^4-diene ligands[11] and of conjugated dienes to pentadienyl ligands.[12] Preliminary investigations of reactions of $(TMM)Fe(CO)_3$ with 2,3-dimethyl-1,3-butadiene and 1,3-butadiene suggest that the former yields a compound analogous to I while the latter yields a tricarbonyl compound, not yet identified.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council (operating and equipment grants to M.C.B.) and Queen's University (graduate fellowship to L.G.) made this research possible.

Supplementary Material Available: Complete tables of atomic positional and thermal parameters, bond lengths and angles, and anisotropic thermal parameters for I (5 pages). Ordering information is given on any current masthead page.

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[6] See Figure 1 for the numbering scheme. ^{13}C NMR resonances (C_6D_6): δ 219.2 (CO), 216.5 (CO), 123.5 (C(5) or C(9)) 109.5 (C(9) or C(5)), 76.7 (C(8)), 64.0 (C(4)), 45.3 (C(3)), 45.2 (C(10)), 39.1 (C(6)), 32.1 (C(7)), 27.4 (C(11)). ^1H NMR resonances (C_6D_6): δ 3.16 (d, H(3A)), 3.07 (dd, H(10A)), 3.04 (dd, H(8)), 2.76 (br s, H(10B)), 2.24 (d, H(4A)), 2.18 (br s, H(3B)), 2.15 (br s, H(4B)), 2.07 (dd, H(6B)), 1.79 (dddd, H(6A)), 1.49 (s, H(11A,B,C)), 1.36 (ddd, H(7A)), 0.66 (dddd, H(7B)); $J_{3A-4A} = 3.3$, $J_{4B-6A} = 1.5$, $J_{6A-6B} = 12.2$, $J_{6A-7A} = 4.8$, $J_{6A-7B} = 14.2$, $J_{6B-7B} = 5.0$, $J_{7A-7B} = 13.2$, $J_{7A-8} = 6.3$, $J_{7B-8} = 10.8$, $J_{8-10A} = 1.5$, $J_{10A-10B} = 1.5$ Hz.

[7] Available as PCMODEL from Serena Software, Bloomington, IN. See: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Adv. Mol. Model.* 1990, *2*, 65.

[8] Crystal Data: $C_{11}H_{14}FeO_2$, $M_r = 234.06$, monoclinic, space group $P2_1/c$, $a = 8.8800\ (12)$ Å, $b = 8.9197\ (12)$ Å, $c = 13.5091\ (17)$, $\beta = 95.642\ (11)°$, $V = 1064.82\ (24)$ Å^3, $Z = 4$, $D_c = 1.460$ g cm^{-3}, $F(000) = 488$, μ(Mo Kα) = 13.86 cm^{-1}, $R = 0.0401$ ($R_w = 0.0466$) for 2440 observed data (298 K, Wyckoff ω scans, $2\theta \leq 55°$, $F \geq 4\sigma(F)$). Data were collected using a Siemens P4 diffractometer (298 K, Mo Kα radiation, $\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects, and the structures were solved using direct methods (SHELXTL PLUS program). Complete details will be published in a full paper.

[9] (a) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 31.3. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* 1989, S1.

[10] (a) Nesmeyanov, A. N.; Kritskaya, I. I. *J. Organomet. Chem.* 1968, *14*, 387. (b) Chenskaya, T. B.; Leites, L. A.; Kritskaya, I. I.; Babakhina, G. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) 1975, 1292.

[11] Green, M.; Lewis, B.; Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* 1975, 1118.

[12] Kreiter, C. G.; Lehr, K. *J. Organomet. Chem.* 1991, *406*, 159.

Oxidative Addition of Germanium–Germanium and Germanium–Chlorine Bonds to $Pt(PEt_3)_3$ and Unexpected Germylene Generation from the Resulting Bis(chlorogermyl)platinum Complex

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Summary: Reactions of $ClMe_2GeGeMe_2Cl$ and Me_2GeCl_2 with $Pt(PEt_3)_3$ proceeded to give *cis*-/*trans*-$(ClMe_2Ge)_2Pt(PEt_3)_2$ (**1**) and *trans*-$(ClMe_2Ge)PtCl(PEt_3)_2$ (**2**), respectively. The structure of *cis*-**1** was determined by crystallography. Thermolysis of a cis/trans mixture of **1** afforded **2** with release of dimethylgermylene, which could be trapped by benzil to give a 1,3-dioxa-2-germa-4-cyclopentene species.

In view of the growing interest in group 14 metal-based materials and reagents,[1] understanding of the reactivities

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[1] (a) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989. (b) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 10. (c) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 11.

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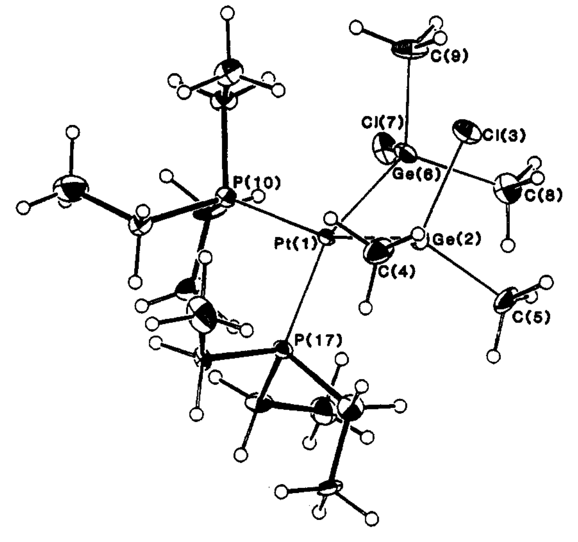

Figure 1. ORTEP drawing of *cis*-1, showing selected atom labeling. Hydrogen atoms are shown as open circles. Selected structural parameters are as follows: Pt(1)–P(10) = 2.350 (4), Pt(1)–P(17) = 2.333 (4), Pt(1)–Ge(2) = 2.4271 (15), Pt(1)–Ge(6) = 2.4327 (15) Å; Ge(2)–Pt(1)–P(10) = 158.39 (10), Ge(6)–Pt(1)–P(17) = 158.62 (10), Pt(1)–Ge(2)–C(5) = 123.7 (5), Pt(1)–Ge(2)–C(4) = 113.63 (25).

of these metal compounds is highly desired. As compared with silicon species, however, the knowledge of reactivities of germanium systems is extremely limited.[2] Herein are reported the first examples of oxidative addition of a Ge–Ge and a Ge–Cl bond to a Pt(0) complex[3–5] and unexpected generation of germylene species upon thermolysis of a bis(chlorogermyl)platinum complex.

When $ClMe_2GeGeMe_2Cl$ was treated with $Pt(PEt_3)_3$ in benzene (or benzene-d_6 for NMR monitoring) at room temperature, selective oxidative addition took place at the Ge–Ge bond to give *cis*- and *trans*-$(ClMe_2Ge)_2Pt(PEt_3)_2$ (1), while the Ge–Cl and Ge–Me bonds remained intact (eq 1).[6,7] From the resulting mixture, *cis*-1 was isolated

$$Pt(PEt_3)_3 + ClMe_2GeGeMe_2Cl \xrightarrow[C_6D_6,\ r.t.]{-\ PEt_3} \underset{1\ (in\ solution)}{cis/trans\text{-}(ClMe_2Ge)_2Pt(PEt_3)_2} \xrightarrow{crystallization} cis\text{-}1 \quad (1)$$

as pale yellow crystals and the structure was confirmed by X-ray crystallography (vide infra).[8] The structure of *trans*-1 could be reasonably assigned[7] by the observation of (a) a virtual coupling of the methylene protons in triethylphosphine with two phosphorus atoms[9] and (b) a rather small value of $^3J_{PtH}$ in $ClMe_2Ge$ ligands (6.5 Hz) and a relatively large value of $^1J_{PtP}$ (2495 Hz), which are consistent with the trans influence of a germyl ligand being higher than that of a phosphine ligand.[10] The selective crystallization of *cis*-1, which has a larger dipole moment than *trans*-1, probably is due to its low solubility in nonpolar hexane. It is interesting to note that the analogous $(ClMe_2Si)_2Pt(PEt_3)_2$, which is obtained from $Pt(PEt_3)_3$ and $ClMe_2SiSiMe_2Cl$, adopts only a cis geometry in benzene-d_6.[3a] Bulky germyl groups, in comparison with the corresponding silyl groups, presumably disfavor the sterically congested cis form in solution.

A similar reaction of $Me_3GeGeMe_3$ did not proceed even at 60 °C, indicating that the cleavage of the Ge–Ge bond is facilitated by the chlorine atoms attached to the germanium atoms, as observed in the reactions of disilanes.[3a]

The structure of *cis*-1 (Figure 1) is distinctly distorted from planarity; the dihedral angle between the PtP_2 and the $PtGe_2$ planes is 28.5°. This deformation is caused by repulsion between the four tertiary (i.e., bulky) ligands and is common for planar d^8 compounds.[11] The steric congestion is only partially reduced by a "tooth-and-cog" gearing of the four ligands. Only one alkyl group of each ligand lies near the Ge_2PtP_2 mean plane, and these groups have larger Pt–X–C (X = P, Ge) angles (124.9° average) than do those projecting away from this plane (111.8° average).

Although crystallized 1 had a cis geometry, dissolution in hydrocarbons such as benzene, toluene, and hexane caused rapid isomerization to give a cis/trans equilibrium mixture.[12] The cis/trans equilibrium is temperature-dependent; ^1H and ^{31}P NMR measurements in toluene-d_8 showed that cis/trans ratios were 39/61 (27 °C), 24/76 (−30 °C), and 13/87 (−60 °C), thermodynamic parameters ΔH and ΔS being estimated at −8.5 kJ/mol and −25 eu, respectively. Addition of triethylphosphine significantly promoted the isomerization; the cis/trans ratios after benzene-d_6 solutions of *cis*-1 (2.4×10^{-3} M) were kept at 20 °C for 4 min were 93/7, 76/24, and 61/39 in the presence of 0, 2, and 6 equiv of added phosphine, respectively. Accordingly, the isomerization may be best explained by the mechanism involving a pentacoordinate intermediate.[13]

When Me_2GeCl_2 was allowed to react with $Pt(PEt_3)_3$, selective addition of a Ge–Cl bond took place at room temperature to give *trans*-$(ClMe_2Ge)PtCl(PEt_3)_2$ (2; eq 2).[14] The reactivity of the Ge–Cl bond is much higher than

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(2) Mackay, K. M.; Nicholson, B. K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel., E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 43.

(3) For our recent studies on the relevant reactions of organosilicon compounds with group 10 and/or 9 metal complexes, see: (a) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447. (b) Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* **1990**, 2107 and references cited therein.

(4) An addition reaction of a Ge–Ge bond in a strained digermacyclopropane to $Pd(PPh_3)_4$ was reported: Tsumuraya, T.; Ando, W. *Organometallics* **1989**, *8*, 2286.

(5) For oxidative addition of Ge–Cl bonds to Pt(II) complexes, see: Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171.

(6) The digermane $ClMe_2GeGeMe_2Cl$ (0.119 mmol) was added to $Pt(PEt_3)_3$ (0.119 mmol) in benzene (1.0 mL), and the resulting mixture was stirred at room temperature for 20 min. The volatiles were removed in vacuo, and the residue was extracted with hexane. Slow cooling of the hexane extract down to −30 °C gave pale yellow crystals of *cis*-1 (0.093 mmol, 78% yield); mp 92–95 °C (under nitrogen). Anal. Calcd for $C_{16}H_{42}Cl_2Ge_2P_2Pt$: C, 27.15; H, 5.99. Found: C, 27.37; H, 5.75. IR (Nujol): 1253 (w), 1224 (w), 1214 (w), 1035 (s), 1004 (w), 828 (m), 802 (m), 762 (s), 717 (s), 632 (w), 578 (m), 565 (m) cm^{-1}.

(7) NMR data for *cis*- and *trans*-1 were obtained using a solution prepared by dissolution of crystallized *cis*-1 in benzene-d_6 (see the text). *cis*-1: ^1H NMR (C_6D_6, TMS) δ 1.22 (s, $^3J_{PtH}$ = 9.9 Hz, 12 H, $GeCH_3$), 0.83 (dt, $^3J_{PH} \approx 2^3J_{HH} \approx$ 15.2 Hz, 18 H, PCH_2CH_3), 1.81 (dq, $^2J_{PH} \approx {}^3J_{HH} \approx$ 7.6 Hz, $^3J_{PtH} \approx$ 15 Hz, 12 H, PCH_2); ^{31}P NMR (C_6D_6, H_3PO_4) δ 15.68 (s, $^1J_{PtP}$ = 2251 Hz). *trans*-1: ^1H NMR (C_6D_6, TMS) δ 1.07 (s, $^3J_{PtH}$ = 6.5 Hz, 12 H, $GeCH_3$), 0.83 (dt, $^3J_{PH} \approx {}^3J_{HH} \approx$ 7.7 Hz, 18 H, PCH_2CH_3), 1.81 (tq, $^2J_{PH} \approx$ 3.2 Hz, $^3J_{HH} \approx$ 7.7 Hz, $^3J_{PtH} \approx$ 21 Hz, 12 H, PCH_2); ^{31}P NMR (C_6D_6, H_3PO_4) δ 15.68 (s, $^1J_{PtP}$ = 2495 Hz).

(8) Crystallographic data for *cis*-1 at −174 °C: a = 10.301 (1) Å, b = 13.676 (2) Å, c = 18.503 (2) Å, and β = 102.71 (1)° with Z = 4 in space group $P2_1/n$. $R(F)$ = 0.0494, $R_w(F)$ = 0.0472 for 2823 observed ($F > 3\sigma(F)$) reflections up to 2θ = 45°, using fixed idealized hydrogens and anisotropic thermal parameters on all non-hydrogen atoms.

(9) Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1967**, 1066.

(10) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(11) Lundquist, E. G.; Streib, W. E.; Caulton, K. G. *Inorg. Chim. Acta* **1989**, *159*, 23.

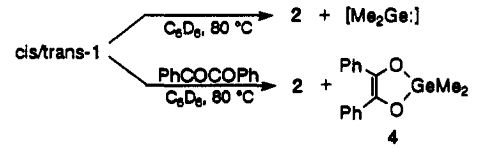
(12) The possibility of similar isomerization was suggested also for $(Ph_3Ge)LPt(PEt_3)_2$ (L = $GePh_3$, $GeMe_3$).[9]

(13) For a review of cis/trans isomerization of square-planar complexes, see: Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

that of the Si–Cl bond since oxidative addition of a Si–Cl bond in Me_2SiCl_2 requires temperatures as high as 90–120 °C.[15]

$$Pt(PEt_3)_3 + Me_2GeCl_2 \xrightarrow[C_6D_6,\ r.t.]{-PEt_3} \underset{\mathbf{2}}{trans\text{-}(ClMe_2Ge)PtCl(PEt_3)_2} \quad (2)$$

Interestingly, thermolysis of **1** also formed **2** with release of dimethylgermylene. Thus, when a benzene-d_6 solution of **1** (cis/trans = 39/61, 8.3 × 10^{-2} M) was heated in a sealed NMR tube at 80 °C with periodical monitoring by ^1H NMR spectroscopy at 20 °C, the proton signals of **2** increased with concomitant decrease of those of **1** (almost constant cis/trans ratio ~ 4/6). After 12 h, **2** was formed in 48% yield at 88% conversion of **1** (eq 3). Germylene trapping experiments using styrene, 2,3-dimethyl-1,3-butadiene, diphenylacetylene, and dimethylphenylsilane failed. However, treatment with phenylacetylene (20 equiv, 80 °C, 2 h) afforded adducts with dimethylgermylene ($Me_2Ge/PhC{\equiv}CH = 1/2$) (**3**),[16] albeit only in trace yields. In addition, benzyl bromide (3 equiv, 80 °C, 2 h) gave the benzylgermyl bromide (12% yield) along with the benzylgermyl chloride (14% yield).[18] Furthermore, benzil (10 equiv, 80 °C, 10 h) could effectively trap the germylene species to give a 1-germa-2,5-dioxa-3-cyclopentene species (**4**, 48% yield)[19] accompanied by **2** (68% yield) (eq 3). These results verify the generation of dimethylgermylene species upon thermolysis.[22,23]



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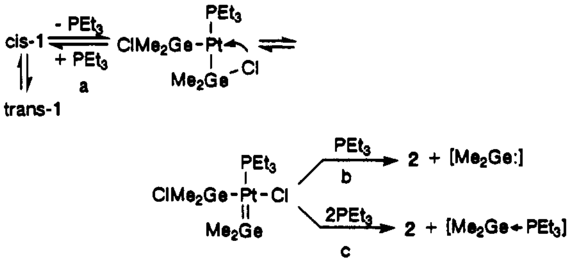
(3)

Concerning the mechanism, a process via α-migration of a chlorine atom leading to a (germylene)platinum intermediate[24] is conceivable. In fact, the structure of *cis*-**1** (Figure 1) shows that a chlorine atom (Cl(7)) is in close proximity of both the platinum center and a phosphine ligand. Accordingly, we propose that *cis*-**1**, which is in equilibrium with *trans*-**1**, undergoes dissociation of the phosphine and α-migration of the chlorine atom (eq 4). In view of the steric congestion and strong trans influence of the germyl ligand[10] in *cis*-**1**, the phosphine dissociation (path a) does not seem to be a crucial step. Indeed, phosphine addition did not inhibit but rather promoted the reaction; the yield of **2** after **1** was heated alone (80 °C, 1 h) was 11%, while it was 46, 46, or 32% after the same treatment in the presence of 1, 2, or 8 equiv of added triethylphosphine, respectively. Although further study is required, this may be rationalized by rate-determining phosphine recoordination (path b) and/or phosphine-assisted abstraction of dimethylgermylene (path c).[25,26] The effect of phosphine strikingly contrasts with the case of *cis*-$(Me_2PhSi)_2Pt(PMePh_2)_2$, in which silylene generation was almost completely suppressed by addition of methyldiphenylphosphine.[27]



(4)

Different from **1**, **2** is thermally stable, and the separately prepared **2** remained unchanged in the absence or presence of triethylphosphine even after heating at 140 °C. Further investigations on the detailed reactivities of (germyl)metal complexes as well as the application of the present results to the development of catalytic reactions[28] will be future subjects.

Acknowledgment. We thank the NSF-STA Summer Institute in Japan program for providing a summer student position to J.A.S. at the National Chemical Laboratory for

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(14) A benzene-d_6 (0.35 mL) solution of Me_2GeCl_2 (0.24 mmol) was added to $Pt(PEt_3)_3$ (0.24 mmol) under nitrogen at room temperature. ^1H NMR spectroscopy of the resulting mixture after 20 min showed that a MeGe–Pt species (1.13 ppm, $^3J_{PtH}$ = 13.5 Hz) cleanly formed with consumption of Me_2GeCl_2. The volatiles were removed in vacuo, and the resulting pale yellow oil was extracted with pentane. Cooling of the pentane extract down to −80 °C gave white crystals of **2** (0.15 mmol, 61% yield); mp 29–30 °C (under nitrogen). ^1H NMR (C_6D_6, TMS): δ 1.13 (s, $^3J_{PtH}$ = 13.6 Hz, 6 H, $GeCH_3$), 0.93 (dt, $^3J_{PH} \approx {}^3J_{HH} \approx$ 8.0 Hz, 18 H, PCH_2CH_3), 1.95 (tq, $2^2J_{PH} \approx {}^3J_{HH} \approx$ 7.0 Hz, $^3J_{PtH} \approx$ 21 Hz, 12 H, PCH_2). ^{31}P NMR (C_6D_6, H_3PO_4): δ 16.69 ($^1J_{PtP}$ = 2524 Hz). IR (neat); 1454 (m), 1411 (m), 1376 (m), 1030 (s), 824 (m), 772 (s), 753 (s), 724 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{36}Cl_2GeP_2Pt$: C, 27.80; H, 6.00. Found: C, 28.14; H, 6.07.

(15) Yamashita, H.; Hayashi, T.; Tanaka, M. Jpn. Kokai Tokkyo Koho, JP 90-794 (to Agency of Industrial Science and Technology of Japan), 1990.

(16) GC, GC–MS, and GC–HRMS analyses showed the formation of three adducts (**3a–c**), although their MS fragmentation patterns did not agree with those reported for 2,5- and 2,4-diphenyl-1-germa-2,4-cyclopentadiene.[17] MS (EI, 70 eV): *m/z* 308 (M^+ for ^{74}Ge), 293 (M^+ −15), 151 (PhGe). The relative intensity values (%) of these fragments are 68, 100, and 35 for **3a**, 100, 97, and 73 for **3b**, and 100, 65, and 36 for **3c**, respectively. HRMS (EI, 70 eV): calcd for $C_{18}H_{18}Ge$ 308.0621, found 308.0602 for **3a** and 308.0615 for **3b** and **3c**.

(17) (a) Barton, T. J.; Nelson, A. J.; Clardy, J. *J. Org. Chem.* **1972**, *37*, 895. (b) Billeb, G.; Neumann, W. P.; Steinhoff, G. *Tetrahedron Lett.* **1988**, *29*, 5245.

(18) The result suggests that bis(germyl)metal species are possible intermediates in the single germylation of organic halides with $ClMe_2GeGeMe_2Cl$, affording germylene-insertion-type products: Reddy, N. P.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1991**, 677. Insertion of Me_2Ge into benzyl bromide has been reported: Köcher, J.; Lehnig, M. *Organometallics* **1984**, *3*, 937.

(19) Although the MS data for **4** were not consistent with the literature values,[20] GC, GC–MS, and ^1H NMR data for **4** were in good agreement with the following data for an authentic sample (a thermally unstable white solid) prepared from benzoin dipotassium salt and Me_2GeCl_2 according to a reported method for its diethylgermylene analogue:[21] ^1H NMR (C_6D_6, TMS) δ 0.30 (s, 6 H, CH_3), 6.9–7.2 (m, 6 H, aromatic H), 7.7–7.8 (m, 4 H, aromatic H); MS (EI, 70 eV, relative intensity) *m/z* 314 (100, M^+ for ^{74}Ge), 284 (59, M^+ − 30), 181 (64, Me_2PhGe), 105 (34, PhCO), 77 (61, Ph); HRMS (EI, 70 eV) calcd for $C_{16}H_{16}GeO_2$ 314.0361, found 314.0361. In addition, the fact that hydrolysis of **4** gave benzoin also supports the structure.

(20) Michels, E.; Neumann, W. P. *Tetrahedron Lett.* **1986**, *27*, 2455.

(21) Lavayssiere, H.; Dousse, G. *J. Organomet. Chem.* **1985**, *297*, C17.

(22) Thermal decomposition reactions of $(Ph_3Ge)_2M(PR_3)_2$ (M = Pd, R = Et; M = Pt, R = Et, Pr) affording $Ph_3GeGePh_3$ and Ph_4Ge were previously reported: (a) Cross, R. J.; Glockling, F. *J. Chem. Soc.* **1965**, 5422. (b) Brooks, E. H.; Glockling, F. *J. Chem. Soc. A* **1966**, 1241.

(23) Analogous methylene elimination from M–CH_2–Cl linkages giving M–Cl (M = Pt, Ru) bonds was reported: (a) McCrindle, R.; Ferguson, G.; Arsenault, G. J.; Hampden-Smith, M. J.; McAlees, A. J.; Ruhl, B. L. *J. Organomet. Chem.* **1990**, *390*, 121. (b) Hubbard, J. L.; Morneau, A.; Burns, R. M.; Nadeau, O. W. *J. Am. Chem. Soc.* **1991**, *113*, 9180.

(24) For a review of (germylene)metal complexes, see: Petz, W. *Chem. Rev.* **1986**, *86*, 1019.

(25) Diorganogermylenes are known to form complexes with a phosphine: Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

(26) We cannot unequivocally exclude a possible alternative route involving reductive elimination of $ClMe_2GeGeMe_2Cl$ from **1**, subsequent redistribution leading to $Cl(GeMe_2)_nCl$ ($n \geq 1$), and oxidative addition of Me_2GeCl_2 to Pt(0) to give *trans*-**2**, although we could not detect $Cl(GeMe_2)_nCl$.

(27) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411.

(28) We and another group recently reported catalytic transformation reactions of Ge–Ge bonds: (a) Reference 4. (b) Hayashi, T.; Yamashita, H.; Sakakura, T.; Uchimaru, U.; Tanaka, M. *Chem. Lett.* **1991**, 245. (c) Reference 18.

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Supplementary Material Available: Tables of crystal data, fractional coordinates and thermal parameters, and bond distances and angles for *cis*-1 (9 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of N-Substituted Amides to Molybdenum(II) Involving N–H Bond Cleavage To Give (η^2-*N*-Acylamido-*N*,*O*)hydridomolybdenum(II) Complexes: X-ray Molecular Structure of the Seven-Coordinate Complex $[MoH\{N(COCH_3)CH_3\}\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]$

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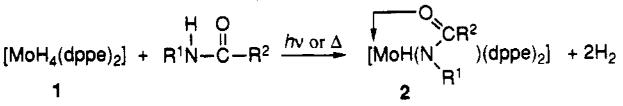
Summary: Photochemical or thermal reaction of $[MoH_4(dppe)_2]$ with *N*-alkylamides R^1NHCOR^2 (R^1, R^2: Me, Me; Ph, Me; Me, H; Ph, H; $(CH_2)_3$; Ph, Ph) in benzene or toluene yielded $[MoH\{N(R^1)COR^2\text{-}N,O\}(dppe)_2]$ as a result of the oxidative addition involving amide N–H bond cleavage (dppe = $Ph_2PCH_2CH_2PPh_2$). The resulting *N*-acylamido complexes have been characterized by means of NMR and IR spectroscopy as well as with an X-ray crystal structure study for R^1, R^2 = Me, Me. Some reactions of the *N*-acylamido complexes, including the oxidation of MeOH to yield a formaldehyde-coordinated complex, are also described.

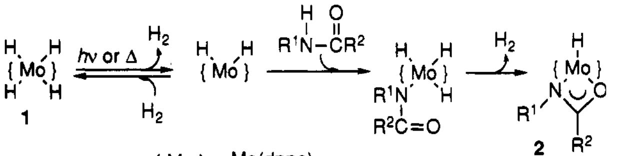
An investigation of the interaction between organotransition metals and organic nitrogen compounds such as amines, amides, and amino acids is intriguing in view of its relevance to biological systems. Among the nitrogen compounds, organic amides are especially important in this respect since they constitute a fundamental component of protein. In contrast to the fairly rich chemistry of transition-metal amido or imido complexes which are synthesized by the reaction of alkali-metal salts of amines with the transition-metal complexes,[1] examples of a direct oxidative addition of the N–H bond of unfunctionalized amines or amides to the transition-metal complexes are surprisingly few.[2] While several examples of the oxidative addition of a highly polarized N–H bond of a cyclic imide such as succinic and phthalic imides have been reported,[3] there has been only one precedent for the oxidative addition of simple amides involving N–H bond cleavage, where (acylamido)hydridoruthenium(II) and -iron(II) complexes are isolated and characterized.[4,5] Here we report the reaction of organic amides with molybdenum polyhydrides to give oxidative-addition products involving nitrogen–hydrogen bond cleavage. Molybdenum is especially important among the transition metals because it is one of the essential metals in biological activity.

Scheme I



R^1,R^2 = CH_3,CH_3 (**a**); C_6H_5,CH_3 (**b**); CH_3,H (**c**); C_6H_5,H (**d**); $(CH_2)_3$ (**e**); C_6H_5,C_6H_5 (**f**)

Scheme II



{ Mo } = $Mo(dppe)_2$

Irradiation for 3–5 h with a 100-W high-pressure mercury lamp at room temperature of a yellow benzene solu-

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(1) See for example: (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

(2) See for example: (a) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (b) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309.

(3) (a) Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254. (b) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1978**, *154*, C37. (c) Ikariya, T.; Takizawa, S.; Shirado, M.; Yoshikawa, S. *J. Organomet. Chem.* **1979**, *171*, C47. (d) Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* **1982**, 907. (e) Kurishima, S.; Ito, T. *Chem. Lett.* **1990**, 1299. (f) Kurishima, S.; Matsuda, N.; Tamura, N.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1991**, 1135.

(4) Schaad, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 1628.

(5) While this paper was in preparation, the reaction of NH_2COR (R = CF_3, Ph) with a ruthenium complex to form N-bonded (acylamido)ruthenium complexes was communicated: Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1146.

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