the ethoxyaminocarbene group has little carbene character and it should be regarded as an O-ethylated carbamoyl group which is linked to the palladium center by a single bond.

Acknowledgment. This work is supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. Financial support from the Toray Science Foundation is gratefully acknowledged.

Supplementary Material Available: Atomic numbering scheme and tables of positional parameters, bond distances and angles, and anisotropic thermal parameters (4 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Thermolytic Rearrangement of *cis*-Bis(phosphine)bis[(trimethylsilyl)methyl]platinum(II) Complexes via *β*-Alkyl Transfer

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Summary: Bis[(trimethylsilyl)methyl]platinum(II) complexes *cis*-$Pt(CH_2SiMe_3)_2L_2$ (L = PEt_3, PPh_2Me, PPh_3) do *not* afford 1-metalla-3-silacyclobutanes via thermolytic γ-C–H migration but instead undergo a novel linkage isomerization, involving β-Si–CH_3 scission and transfer, to afford the unusual methylplatinum(II) products *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$. η^2-Silylene complexes are likely intermediates.

(Trimethylsilyl)methyl and neopentyl derivatives of transition metals were among the forefront of development in alkylmetal chemistry when it was realized that β-hydrogen migration was a major labilizing pathway.[1] More recently, a number of neopentylmetal complexes have been reported to undergo intramolecular aliphatic γ-C–H activation and transfer, generating 3,3-dimethylmetallacyclobutanes.[2] The mechanism has been explored in detail for platinum complexes. (Trimethylsilyl)methyl analogues often react similarly[2a,b,d,e,3] though, in general, less readily. It seems to be assumed widely that the mechanistic controls on the two systems are likely to be the same, irrespective of metal. Relatedly, several neophyl [CH_2CMe_2Ph] complexes rearrange by distal aromatic H migration to form 3,3-dimethylmetallaindans.[2e,4] Again, mechanisms are best understood for platinum derivatives[4c,d] and the corresponding reactions of sila-neophyl [CH_2SiMe_2Ph] species are slower.[5] Organo-f-block metal compounds—notably $Th(CH_2EMe_2R)_2(\eta^5\text{-}C_5Me_5)_2$ [E = C, Si; R = Me, Ph]—show similar reactivity trends.[6] Our interest in understanding the relative inertness of β-sila-alkyl systems has prompted investigation of a range of bis[(trimethylsilyl)methyl]platinum(II) complexes.[7] The unexpected results of thermolytic rearrangement of several of these with monodentate tertiary phosphine ligands demonstrate that mechanistic analogies cannot be assumed, even for the same metal. In contrast to their neopentylplatinum analogues, they do *not* yield metallacycles. Thermolysis of toluene-d_8 solutions of the complexes $Pt(CH_2SiMe_3)_2L_2$ [**1**, L = PEt_3, PPh_2Me, PPh_3] results in quantitative rearrangement to novel methyl({[(trimethylsilyl)methyl]dimethylsilyl}methyl)platinum(II) complexes, *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$ (**8**), identified by their ^1H, ^{13}C, and ^{31}P NMR spectroscopic characteristics and by mass spectrometric and elemental analyses of the two isolable examples (where L = PEt_3, the pure product could not be recovered). The structure of the triphenylphosphine derivative has been confirmed by X-ray diffractometry.[8] Reaction of the trimethylphosphine complex requires more vigorous conditions, and though the predominant pathway is analogous, secondary and/or competitive reactions are apparent.

The asymmetric geometry of the products is most clearly evident from the $^{31}P\{^1H\}$ NMR data.[9] The $^{13}C\{^1H\}$ spectra allow unequivocal assignment of the structure.[10] Two distinct Pt–CH_n resonances are observed. Of these (from ADEPT measurements) the lower field resonance arises from a Pt–CH_2 grouping, while the higher field signal clearly corresponds to Pt–CH_3. Two Si–CH_3 environments are also evident, one displaying $^3J_{Pt\text{-}C}$ interaction (comparable to that in the parent complex **1**) and a second, more intense, with no observable coupling. A further aliphatic carbon showing $^3J_{Pt\text{-}C}$ coupling is attributed to a Si–CH_2 group.

An important aspect of product analysis in this instance is the origin of the methyl group bound ultimately to platinum. Though rearrangement of the selectively deuterated complex *cis*-$Pt[CH_2Si(CD_3)_3]_2(PPh_2Me)_2$ is slower (vide infra), it generates an exactly analogous product whose $^{13}C\{^1H\}$ NMR spectrum reveals the presence *only* of Pt–CD_3 and Pt–CH_2–Si groups. Superficially, then, the

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(9) ^{31}P data for *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$ (in toluene-d_8; δ in ppm relative to external 60% H_3PO_4; J in Hz): L = PEt_3, $\delta(P_1) = 8.71$, $^1J(P_1\text{–}Pt) = 1976$, $\delta(P_2) = 6.84$, $^1J(P_2\text{–}Pt) = 1879$, $^2J(P_1\text{–}P_2) = 12$; L = PPh_2Me, $\delta(P_1) = 5.26$, $^1J(P_1\text{–}Pt) = 1943$, $\delta(P_2) = 5.26$, $^1J(P_2\text{–}Pt) = 1870$, $^2J(P_1\text{–}P_2) = 11$; L = PPh_3, $\delta(P_1) = 28.9$, $^1J(P_1\text{–}Pt) = 1955$, $\delta(P_2) = 26.0$, $^1J(P_2\text{–}Pt) = 1921$, $^2J(P_1\text{–}P_2) = 11$; L = PMe_3, $\delta(P) = -26.9$, $^1J(P_1\text{–}Pt) = 1952$, $\delta(P_2) = -25.8$, $^1J(P_2\text{–}Pt) = 1886$, $^2J(P_1\text{–}P_2) = 11$.

(10) Selected ^{13}C data for *cis*-$Pt(CH_3)(CH_2SiMe_2CH_2SiMe_3)L_2$ (in chloroform-d; $\delta(C)$ in ppm relative to external TMS; J in Hz). (a) L = PPh_2Me: Pt–CH_3, $\delta(C) = 4.81$, $^1J(C\text{–}Pt) = 596$, $^2J(C\text{–}P_{trans}) = 104$, $^2J(C\text{–}P_{cis}) = 13$; Pt–$CH_2$, $\delta(C) = 11.55$, $^1J(C\text{–}Pt) = 558$, $^2J(C\text{–}P_{trans}) = 85$, $^2J(C\text{–}P_{cis}) = 6$; $Si(CH_3)_3$, $\delta(C) = 1.74$; $Si(CH_3)_2$, $\delta(C) = 4.92$, $^3J(C\text{–}Pt) = 26$; Si–CH_2, $\delta(C) = 8.54$, $^3J(C\text{–}Pt) = 31$. (b) L = PPh_3: Pt–CH_3, $\delta(C) = 7.75$, $^1J(C\text{–}Pt) = 604$, $^2J(C\text{–}P_{trans}) = 97$, $^2J(C\text{–}P_{cis}) = 8$; Pt–$CH_2$, $\delta(C) = 14.05$, $^1J(C\text{–}Pt) = 645$, $^2J(C\text{–}P_{trans}) = 80$, $^2J(C\text{–}P_{cis}) = 5$; $Si(CH_3)_3$, $\delta(C) = 1.99$; $Si(CH_3)_2$, $\delta(C) = 6.28$, $^3J(C\text{–}Pt) = 20$, Si–CH_2, $\delta(C) = 8.80$, $^3J(C\text{–}Pt) = 27$.

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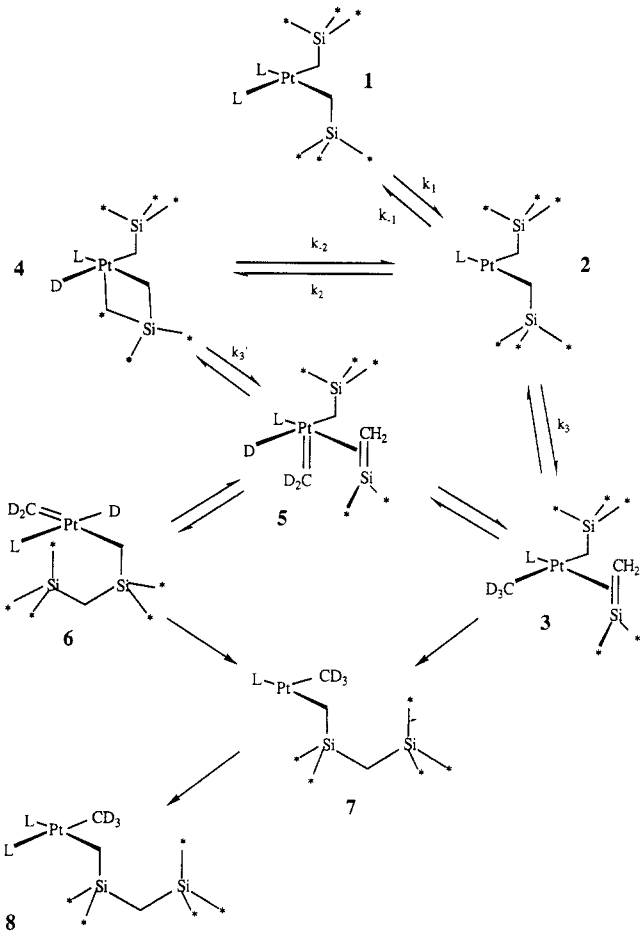
rearrangement features an effective β-methyl migration from silicon. Though rare for d-block metals, β-alkyl transfers have been observed, notably in organoplatinum(II) systems which not only lack transferable hydrogen but also have the impetus of strained alicyclic systems incorporating the β-carbon.[11] Recently, an apparent β-methyl migration has been induced in the reaction of $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_3)Br$ with AgF (or $AgBF_4$) to yield $Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CH_2SiMe_2F)Me$.[12] Mechanistic information is lacking, but it seems likely that the halophilicity of Si is a major stimulus. Generation of $M(\eta^5\text{-}C_5H_5)(CO)_3Me$ [M = Mo, W] from reaction of $Na[M(\eta^5\text{-}C_5H_5)(CO)_3]$ with Me_3SiCH_2I was shown *not* to have resulted from methyl migration.[13]

Three variation studies have been employed to illuminate the mechanism of these rearrangements, which were kinetically first order for at least 3 half-lives.[14] (1) The temperature dependence of k_{obs} for each of *cis*-$Pt(CH_2SiMe_3)_2L_2$ conforms linearly to the Arrhenius relationship. $\Delta H^{\ddagger}_{obs}$ (at 105 °C) is 140–170 $kJ{\cdot}mol^{-1}$ and $\Delta S^{\ddagger}_{obs}$ is in the range +30 to +120 $J{\cdot}mol^{-1}{\cdot}K^{-1}$. (2) The presence of free phosphine markedly reduces the rearrangement rate of all three complexes. Plots of $1/k_{obs}$ versus phosphine concentration are linear with nonzero intercepts. No $Pt(CH_2SiMe_3)_2L_3$ species were detectable. (3) Rearrangement of *cis*-$Pt[CH_2Si(CD_3)_3]_2L_2$ is uniformly slower than that of the undeuterated analogue. The small but significant deuterium isotope effect k^H_{obs}/k^D_{obs} (1.40 ± 0.2) is essentially independent of the nature of L.

The data are most consistent with a pathway in which preliminary phosphine dissociation is a prerequisite—as is often the case for rearrangements in d^8 systems.[2g,4c,15] Values estimated for k_1 from $[L]/k_{obs}$ plots[16] are uniformly greater than k_{obs} and suggest that this first step is not rate-limiting. The data do not yet allow unambiguous delineation between alternative paths in which the new Pt–C bond results from C–H or C–Si activation [Scheme I] although participation by α-hydrogen transfer[17] can be excluded. The relatively small isotopic inhibition may be (i) a secondary effect on direct β-methyl migration [k_3] or (ii) a primary effect on γ-hydrogen transfer, partly diluted as a result of a phosphine reassociation [k_{-1}] rate which is significant compared with that of the successive step(s) [k_2, etc.].[4c] Alkyl migration [k_3] provides the simplest explanation for the specificity demonstrated by the labeling experiment; regiospecific migration of the remaining (trimethylsilyl)methyl group to Si in the η^2-silylene intermediate **3** would be in accord with the relative electrophilicity of the Si site. Related η^2-silylene–Ru complexes (via β-Si–H transfer) have been identified recently,[18] but the general reactivity of such species has yet to emerge. Alternatively, C–H transfer generates the metallacyclobutane **4**. Increased ring strain might account for reactivity distinct from that of its carbon analogue.[2g] Instead, **4** may favor cycloreversion of the type established for metallacyclobutane derivatives,[19] affording **5** (with both an alkylidene and an η^2-silylene ligand) which, in turn, could rearrange to **3** or to **6** by alternative migratory insertions. Ring opening of **4** must be highly regiospecific to accommodate the labeling result, but the inherent asymmetry of this complex might ensure such selectivity. We are engaged in experiments aimed at exploring the scope of this novel rearrangement and further clarifying its mechanism.

Scheme I[a]



[a] The asterisk indicates a perdeuterated carbon site.

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(14) Representative rate data (k_{obs}): L = PEt_3, $k_{105} = 9.45 \times 10^{-6}\ s^{-1}$; L = PPh_2Me, $k_{105} = 1.22 \times 10^{-5}\ s^{-1}$; L = PPh_3, $k_{105} = 3.35 \times 10^{-5}\ s^{-1}$. Notably, the triethylphosphine complex is more thermolytically labile than its neopentyl analogue (cf. ref 2g).

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(16) Assuming steady-state concentrations for the tricoordinate (and any subsequent) intermediate, the relation between k_{obs} and k_1 (the phosphine-dissociation rate; Scheme I) is

$$1/k_{obs} = 1/k_1 + K[L]$$

(where K is a composite of rate constants for subsequent steps and phosphine reassociation; cf. ref 2g and 4c).

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Acknowledgment. We are indebted to Sue Johnson, Dick Sheppard, and Dr. John Arnold for high-field NMR measurements and to Prof. T. D. Tilley for access to the results in ref 18 prior to their publication. We thank the SERC for the award of a studentship (to S.K.T.) and Prof. S. V. Ley for use of his Chemdraw 2 program, and we are ever grateful to Johnson Matthey plc, for their continued support through generous loans of platinum.

Reactions of $(CO)_5Cr{=}C(Me)N(CH_2CH_2)_2$ with Enynes: Mechanistic Insight and Synthetic Value of Changing a Carbene Donor Group from Alkoxy to Dialkylamino

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Summary: Reactions of the title carbene complex (**10**) with 1,6- and 1,7-enynes are described and contrasted with the results of the 1-*methoxy*ethylidene analogues. The more strongly electron-donating pyrrolidino substituent simultaneously provides considerable mechanistic insight and leads to a more generally useful synthetic tool for the preparation of bicyclic cyclopropanes.

The reaction of (1-*methoxy*ethylidene)pentacarbonyl chromium (1) with 1,6- and 1,7-enynes (2) was recently described by us.[2] The principal products (see Scheme I) included bicyclic cyclopropanes (3), bicyclic cyclobutanones (4), furans (5), and metathesized dienes (6). We proposed several mechanistic branch points: (i) the vinylogous methoxycarbene complex 7 (X = OMe) could engage the now internal alkene either before (path a) or after (path b) carbon monoxide insertion leading, respectively, to metallacyclobutane 8 or the vinylketene complex 9, (ii) the metallacyclobutane 8 could reductively eliminate to cyclopropane 3 (path c) or consummate metathesis by producing 6 (path d), and (iii) the vinylketene complex 9 could undergo net 2 + 2 cycloaddition to give the cyclobutanone 4 (path e) or rearrange to the furan 5 (path f).[3] With the hope of tailoring the reaction to only provide the useful vinylcyclopropanes 3 by avoiding path b, we have examined related reactions using (1-*pyrrolidino*ethylidene)-pentacarbonyl chromium (10) and now describe those results. This complex and the intermediates derived therefrom should exhibit greater back-bonding between chromium and carbon monoxide and, therefore, a reduced propensity for CO insertion into 7.[4] The anticipated result was the quenching of path b; such is the case.

Scheme I

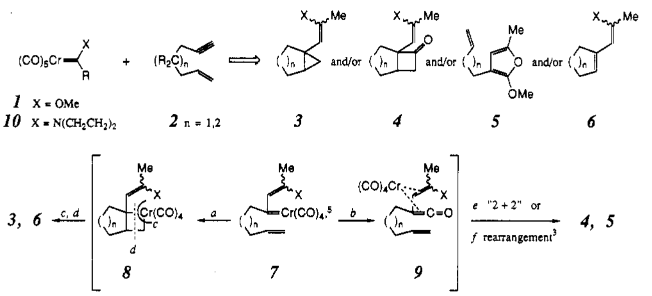
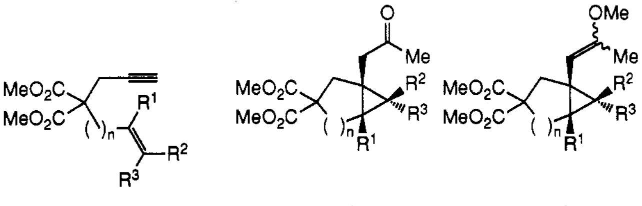


Table I



11 *12* *13*

11-13 a-e	R^1	R^2	R^3	n	Yield[a] of *12* from 10	Yield[a] of *13* from 1 (ref 2)
a	H	H	H	1	88%[b] (76%)[b]	69%
b	Me	H	H	1	(58%)	22%[c]
c	H	H	Me	1	(62%)	2%[d]
d	H	Me	H	1	(64%)	not done
e	H	H	H	2	79% (61%)	46%[e]

a) yields are of MPLC-purified product except those in parentheses which are for material sequentially purified by MPLC and then HPLC b) ~5 mmol scale, all others ~0.5 mmol scale c) 30% cyclobutanone also formed d) 6% cyclobutanone, 30% metathesized diene, and 7% furan formed e) 20% furan formed

When the series of enynes **11a–e** was exposed to the pyrrolidinocarbene **10** in refluxing toluene[6] ([**10**] ≈ 0.7 M, ~1.3 equiv of **11**, 1 h, 120 °C external bath, sealed vessel), the ketocyclopropanes[7] **12a–e** were the only products observed upon inspection of the crude product mixture by ^1H NMR analysis and isolated after MPLC/HPLC on silica gel. As the data in Table I indicate, the yields of cyclopropane **12** using the aminocarbene complex **10** were essentially independent of the degree of alkene substitution

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(1) Fellow of the Alfred P. Sloan Foundation, 1985–1989.

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(4) (a) Cf. reactions of 1 (but with Me replaced by Ph and X = NR_2) with alkynes to generate indenes rather than naphthols:[5] Yamashita, A. *Tetrahedron Lett.* **1986**, *27*, 5915. (b) For a photochemically induced ketene formation from an amino-bearing carbene see: Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

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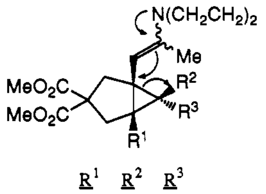
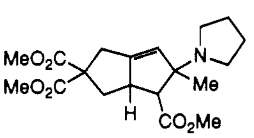
(6) THF, benzene, toluene, and DMF[4a] are all acceptable solvents for the reaction of **10** + **11a**.

(7) ^1H NMR analysis of the crude product mixture before chromatography or of solutions of reactions carried out in C_6D_6 gave no indication of the expected enamine intermediates **i** (cf. ref 4a). Circumstantial evidence that enamine formation is indeed occurring is found in the reaction of **10** with **11** (R^2 = CO_2Me, R^1/R^3 = H) at 120 °C which gave the bicyclo[3.3.0]octane **ii** in 53% yield and as a single diastereomer. This is best envisioned as arising via a thermodynamically controlled vinylcyclopropane rearrangement of the "push-pull" activated enaminoester intermediate **iii**. In fact, a C_6D_6 solution of ketone **12** (R^2 = CO_2Me, R^1/R^3 = H)[2] and excess pyrrolidine at 80 °C resulted after 3 h in clean conversion (^1H NMR) to the rearranged product **ii** [cf.[2] **1** + **11** → **13** (R^2 = CO_2Me, R^1/R^3 = H) in 64%].



	R^1	R^2	R^3
i	H or alkyl		
iii	H	CO_2Me	H



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