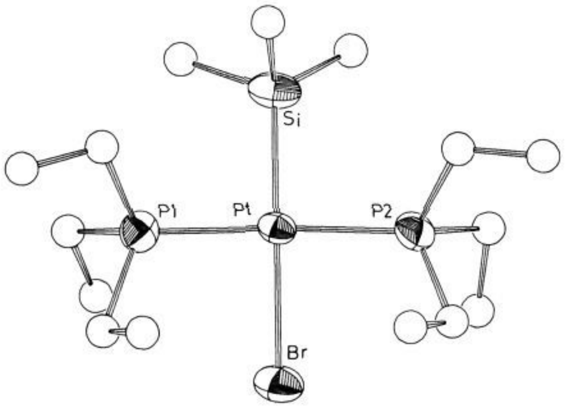

Figure 1. ORTEP drawing of the molecular structure of *trans*-Me$_3$SiPtBr(PEt$_3$)$_2$ (**1**). Selected interatomic distances (Å): Pt–Si, 2.330 (17); Pt–Br, 2.604 (6); Pt–P1, 2.299 (15); Pt–P2, 2.296 (15).

tion-metal bonds are usually anticipated to be more stable than the carbon analogues.[8] These considerations have prompted us to reinvestigate the reactions of halosilanes with metal complexes. We wish to report herein the first examples of the oxidative addition of Si–X bonds to zero-valent platinum complexes.

The reactions were conducted in sealed NMR tubes with benzene as a solvent[9] and were monitored by means of ^{1}H NMR. PtL$_4$ (L = PPh$_3$, PMe$_2$Ph) and Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$ did not react with Me$_3$SiBr even at elevated temperatures up to 120 °C. However, when Pt(PEt$_3$)$_3$ was subjected to the reaction with Me$_3$SiBr, the color changed from orange to yellow after heating at 90 °C for 2 h. In addition, new ^{1}H NMR signals emerged at 0.73, 0.59, and 0.45 ppm, the relative intensity being about 1:4:1. The signals at 0.73 and 0.45 ppm are considered to be the satellite arising from ^{1}H–^{195}Pt coupling of the H$_3$C–Si–Pt moiety of the product.[10] The solvent and the excess halosilane in the reaction mixture were removed, and the residue was extracted with pentane. When the pentane solution was slowly cooled to −50 °C, pale yellow needles were obtained. Single-crystal X-ray diffraction analysis revealed the structure shown in Figure 1. Thus, oxidative addition of the Si–Br bond of Me$_3$SiBr to Pt(PEt$_3$)$_3$ really took place, and *trans*-Me$_3$SiPtBr(PEt$_3$)$_2$ (**1**) was formed.[12]

$$\mathrm{Me_3Si{-}Br + Pt(PEt_3)_3 \xrightarrow{-PEt_3} \mathit{trans}\text{-}Me_3SiPtBr(PEt_3)_2}$$

On the basis of the thermochemical considerations of the reactions of platinum(0) complexes with organo group IV metal halides, Eaborn et al. predicted that, in the oxidative addition of organohalosilanes, the cleavage of the Si–C bond would be preferable to that of the silicon–halogen bond.[13] However, the present result shows that Pt(PEt$_3$)$_3$ selectively undergoes the insertion into the Si–Br bond and that Me$_3$SiBr behaves like organic halides. The yield of **1** was estimated to be about 90% from the ^{1}H NMR spectrum of the reaction mixture. The structure of **1** is notable in that the distance of the Pt–Br bond (2.61 Å, average value of two Pt–Br bonds) is longer than that of *trans*-PtBr$_2$(PEt$_3$)$_2$[14] or *trans*-PtHBr(PEt$_3$)$_2$[15] (2.428 or 2.56 Å, respectively). The result is consistent with the strong trans influence of the Me$_3$Si group[16] as compared with the bromide or hydride ligand.

In place of Pt(PEt$_3$)$_3$, Pt(PEt$_3$)$_4$ also gave the same product when treated with Me$_3$SiBr, though the reaction rate was lower. Me$_3$SiI reacted more easily with Pt(PEt$_3$)$_3$ than Me$_3$SiBr and afforded *trans*-Me$_3$SiPtI(PEt$_3$)$_2$ (**2**).[17] Me$_3$SiCl, however, did not react with Pt(PEt$_3$)$_3$ even at 120 °C, probably because of the strong Si–Cl bond (98 kcal/mol for Me$_3$SiCl bond)[6] as compared with the Si–Br bond. The treatment of Pt(PEt$_3$)$_3$ with Me$_2$PhSiBr and the treatment of Pt(PMe$_3$)$_4$ with Me$_3$SiBr also showed new ^{1}H NMR signals which were considered to arise from the formation of Si–Pt bonds. In any reactions described herein, formation of disilanes was not observed in ^{1}H NMR, though the formation of Me$_3$SiSiMe$_3$ was reported in the reaction of Pd(PPh$_3$)$_4$ with Me$_3$SiX (X = Cl or Br).[18]

In conclusion, this paper has established the first example of the oxidative addition of Si–X bond. Further investigations using other metal complexes and halosilanes as well as mechanistic studies are now under way.

Registry No. 1, 114595-43-6; **2**, 114595-44-7; Me$_3$SiBr, 2857-97-8; Pt(PEt$_3$)$_3$, 39045-37-9; Pt(PEt$_3$)$_4$, 33937-27-8; Me$_3$SiI, 16029-98-4; Me$_2$PhSiBr, 13247-99-9; Me$_3$SiCl, 75-77-4.

Supplementary Material Available: Crystal data for **1**, microanalytical data for **1** and **2** and tables of atomic coordinates, thermal parameters, and bond lengths and angles for **1** (6 pages); listing of structure factor amplitudes for **1** (9 pages). Ordering information is given on any current masthead page.

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[9] Typical reaction condition: platinum complex 0.15 mmol, halosilane 0.45–0.60 mmol, benzene 0.3 mL, 90–120 °C.

[10] The coupling constant of ^{1}H–^{195}Pt is 25.2 Hz which is similar to the value reported for *trans*-Me$_3$SiPtCl(PEt$_3$)$_2$ (24.6 Hz).[11]

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[12] **1**: mp 58–60 °C; ^{1}H NMR (benzene) 0.55, 0.69, 0.83 (1:4:1) (s each, 9 H, CH$_3$Si, $J_{\text{H-C-Si-Pt}}$ = 25.2 Hz), 1.02–1.45 (m, 18 H, PCH$_2$CH_3), 1.84–2.56 (m, 12H, PCH$_2$); IR (Nujol, cm^{-1}) 1236 w, 1038 s, 840 s, 768 m, 742 m, 618 w.

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[17] **2**: mp 79–80 °C; ^{1}H NMR (benzene) 0.52, 0.65, 0.78 (1:4:1) (s each, 9 H, CH$_3$Si, $J_{\text{H-C-Si-Pt}}$ = 23.4 Hz), 0.97–1.47 (m, 18 H, PCH$_2$CH_3), 1.98–2.61 (m, 12 H, PCH$_2$); IR (Nujol, cm^{-1}) 1234 w, 1038 s, 838 s, 760 m, 720 m, 618 w.

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The Remarkably Low Second pK_a of 1-Naphthylacetic Acid. Lithium Ion Pair Acidity in Tetrahydrofuran[1]

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Dianions derived from carboxylic acids (carboxylates deprotonated at the α carbon) have proven to be synthetically useful enolate equivalents in a number of carbon–carbon bond-forming reaction sequences.[2–14] They are readily prepared by the met-

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Table I. Lithium Ion Pair p*K* of Lithium 1-Naphthylacetate, **2**, in THF at 25 °C

entry	10^3[**2**][a]	10^4[**3**][a]	p*K*[b]
A	1.38	0.648	22.13
B	2.25	0.642	22.05
C	1.38	0.738	22.12
D	2.50	0.821	21.97
E	4.02	3.02	21.83
F	3.59	3.16	21.82
G	4.65	4.08	21.76
H	2.90	5.71	21.73
I	3.77	6.38	21.74
J	3.39	9.36	21.66
K	2.75	11.6	21.66
L	2.33	11.4	21.62
M	5.20	14.5	21.65
N	2.44	15.6	21.45
O	3.07	17.3	21.54
P	10.6	8.22	21.99
Q	12.3	6.29	22.12
R	14.4	2.00	22.70

[a] Concentrations in M. [b] Measurements A, C, L, N, O against 9-*n*-butylfluorene (BuFl), p*K* = 22.36 (Gronert, S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2836). Measurements B, D–F, I–K, M, P–R against 9-benzyl-9-*H*-benzo[*def*]fluorene (BnMP), p*K* = 21.35.[19] Measurement G against 9-benzylfluorene (9-BnFl), p*K* = 21.36.[19]

alation of the parent acid with 2 equiv of a strong bulky base, such as lithium diisopropylamide, and allow facile synthesis of useful and unusual acid derivatives such as α-hydroperoxy acids,[10] highly substituted diacids,[14] β-keto acids,[6] and lactones.[12] Although the metal salts of carboxylic acid dianions are widely used in synthesis, little is known about their solution structure and stability. A computed structure is available for monomeric lithium lithioacetate,[15] but Bauer and Seebach[16] have shown that the dilithio salt of a model carboxylic acid is present as an aggregate in tetrahydrofuran (THF) at −108 °C. NMR studies of the dilithio salts of arylacetic acids indicate that much of the negative charge is localized on the oxygens, and therefore resonance from **1** is important.[17] We have shown previously that related ion-triplet

$$\underset{\mathbf{1}}{\mathrm{RCH{=}CO_2{}^{2-}\text{-}2Li^+}}$$

structures have enhanced coulombic stability.[18] We report a study of the ion pair acidity of such salts that makes use of our previously established lithium scale in THF.[19]

Initial studies with fluorene-9-carboxylic acid showed that its second ion pair p*K* was too low for the present scale; it is estimated as <13 because 1,3-diphenylindene failed to quench its dianion.[20,21] Considering that fluorene has an ion pair of p*K* of 22.75,[21,22] the CO_2Li group has an acidifying effect of at least 10 p*K* units. Further studies were made with the 1-naphthylacetic acid system because its salts have the necessary solubilities, spectra, and equilibration rates. In THF, lithium 1-naphthylacetate, **2**, is colorless, but the dilithium salt **3** has a visible absorbance at 442 nm (ε = 10 400). Table I summarizes the p*K* measurements with three indicators. The variation of the p*K* values demonstrates that the observed p*K* is dependent on the concentrations of the salts.[21] At higher dilithio salt concentrations, lower p*K* values are observed (entries A–O), and at higher monolithio salt concentrations, higher p*K* values are observed (entries E–J and P–R). This type of concentration dependence is consistent with both the mono- and dilithio salts being present as aggregates in THF.

If the average aggregations are effectively constant as $(\mathbf{2})_n$ and $(\mathbf{3})_m$, eq 1 may be derived based on an earlier analysis[21]

$$\log K_{\mathrm{obsd}} = [(m-1)/m] \log [\mathbf{3}] + [(1-n)/n] \log [\mathbf{2}] + C \qquad (1)$$

in which K_{obsd} = [**3**][IndH]/[**2**][Ind-Li]. This three-parameter equation gives values of approximately 2 and 3 for *m* and *n*, the average aggregation numbers for **3** and **2**, respectively. The analysis is oversimplified because it does not account for mixtures of aggregate types (dimer ⇄ tetramer) or mixed aggregates (**2·3**). Accordingly, the fit is only fair (residuals of about 0.1–0.2 p*K* units). Nevertheless, it does show that aggregates are involved and that the derived "p*K*" values should be regarded only as "effective p*Ks*" valid only for the concentration regions measured. This aspect of acidity measurements, namely that the acidities involving aggregated species are concentration dependent, is often neglected and should be given wider recognition.

The resulting effective acidity of the lithium carboxylate is remarkably high. Comparison with the corresponding ester would be instructive, but the p*K* of a naphthylacetate ester is not yet available; however, the p*K* of *tert*-butyl phenylacetate on the same lithium ion pair scale is 18.7.[22,23] Substitution of the α-naphthyl for the phenyl group should not change this value by more than 1–2 p*K* units.[24] Thus, the effective p*K* of the lithium salt, which involves aggregates and to which aggregation energies undoubtedly contribute significantly, is only a few units higher than that of a corresponding ester in which only monomers are involved; that is, the aggregated $-CO_2Li$ substituent provides nearly as much carbanion ion pair stabilization as the common acidifying substituents, $-CO_2R$, $-CN$, and $-SO_2R$.[23]

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Synthesis of $(PCy_3)_2Cr(CO)_3$ and Its Reactions with Hydrogen, Nitrogen, and Other Ligands

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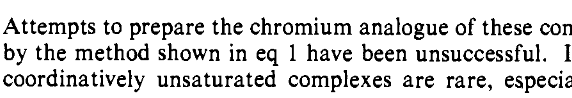
The recent discovery by Kubas and co-workers of the complexes $M(CO)_3(PR_3)_2$ (M = Mo, W, R = C_6H_{11}, *i*-C_3H_7) was of special significance since they were the first complexes shown to bind molecular hydrogen.[1] These complexes are readily prepared from the cycloheptatriene tricarbonyl complexes as shown in eq 1 below.



(1)

Attempts to prepare the chromium analogue of these complexes by the method shown in eq 1 have been unsuccessful. Isolable coordinatively unsaturated complexes are rare, especially for

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