Synthesis and Reactivity of Cationic (η^3-Butadienyl)platinum Complexes

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Summary: (2-η^1-Butadienyl)platinum(II) complexes can be obtained by reaction of [Pt(C_2H_4)(PPh_3)$_2$] with either chloroprene or 4-chloro-3-methylbuta-1,2-diene. Treatment of these complexes with $AgPF_6$ provides direct access to the cationic η^3-butadienyl complexes [Pt{η^3-CH_2:C(R):C:CH_2}(PPh_3)$_2$][PF_6] (R = H, Me), which surprisingly are attacked by the soft carbon nucleophile K[CH(CO_2Me)$_2$] at the central carbon atom of the allylic moiety to form methyleneplatinacyclobutanes. These are unusual molecules that on thermolysis afford Pt(0) methylenecyclopropane complexes.

Although there have recently[1-7] been a number of publications concerned with the synthesis and structures of mononuclear transition-metal complexes carrying η^3-butadienyl ligands, there have been few reports[7] of reactivity studies with these unusual molecules. Deriving from the formal relationship with the reactive cation [Pd(η^3-allyl)(PPh_3)$_2$]$^+$, one group of complexes, which we identified as being of potential interest, were the cations [M(η^3-butadienyl)(PPh_3)$_2$]$^+$ (M = Ni, Pd, Pt). Although one example, the platinum complexes [Pt{η^3-CH(Ph):C(Ph):C:CH_2}(PPh_3)$_2$][BF_4], has previously[3] been prepared by a novel ring-opening reaction of the methyldiphenylcyclopropenium cation with [Pt(C_2H_4)(PPh_3)$_2$], it became swiftly apparent, however, that a more general synthetic approach was required if this chemistry was to be developed further. In this paper we describe a synthesis of wide-ranging scope together with an initial study of the reactivity of the cations [Pt{η^3-CH_2:C(R):C:CH_2}(PPh_3)$_2$][PF_6] (R = H, Me).

Addition of a stoichiometric quantity of chloroprene to a THF solution of [Pt(C_2H_4)(PPh_3)$_2$] gave after $^1/_2$ h a red solution, gradually becoming pale yellow upon prolonged (1 day) stirring at room temperature. Workup by crystallization afforded colorless air-stable crystals of the Pt(II) η^1-butadienyl complex **1** (60%) and variable amounts of *cis*-[$PtCl_2$(PPh_3)$_2$]. In chloroform as solvent the reaction proceeded more rapidly (2 h), giving only **1** in higher yield (85%). Examination of the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra[8] showed the structure of **1** to be as illustrated in Scheme I, it being assumed that the plane of the 2-η^1-butadienyl ligand lies perpendicular to the PtCl·L_2 plane. An alternative synthetic route was provided by the reaction (room temperature, 20 min, THF) of 4-chloro-3-methylbuta-1-2-diene with [Pt(C_2H_4)(PPh_3)$_2$], which led to the rapid formation of **2** (see Scheme I) in high yield (89%), the colorless crystalline material again being characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.[8] With the progress of this reaction assessed by in situ ^{1}H NMR analysis, it was observed that at −30 °C the initial product is the *cis*-η^1-butadienyl species **3**, isomeric with **2**, and that as the mixture is warmed to room temperature a quantitative isomerization reaction occurs to give the isolated

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(8) Selected spectroscopic data for compound **1**: ^{1}H NMR (CD_2Cl_2) δ 7.80–7.35 (m, 30 H, *Ph*$_3$P), 5.67 (dd, 1 H, H^e, J_{ed} = 2.4, J_{ec} = 16.9 Hz), 5.33 (dd, 1 H, H^c, J_{ce} = 16.9, J_{cd} = 10.0, $J_{\text{H-Pt}}$ = 64.8 Hz), 5.11 (s, 1 H, H^b, $J_{\text{H-Pt}}$ = 126.2 Hz), 4.69 (s, 1 H, H^a, $J_{\text{H-Pt}}$ = 67.1 Hz), 4.39 (dd, 1 H, H^d, J_{dc} = 10.0, J_{de} = 2.1 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 148.6 (t, C^2, $J_{\text{C-P}}$ = 8.4 Hz), 147.6 (s, C^3, $J_{\text{C-Pt}}$ = 40.4 Hz), 135.8–127.8 (*Ph*$_3$P), 121.8 (br s, C^4), 116.6 (s, C^1, $J_{\text{C-Pt}}$ = 61.0 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 25.1 (s, $J_{\text{P-Pt}}$ = 3166 Hz). Compound **2**: ^{1}H NMR (CD_2Cl_2) δ 7.77–7.36 (m, 30 H, *Ph*$_3$P), 5.99 (br d, H^e, J_{ce} = 3.2 Hz), 5.18 (s, 1 H, H^b, $J_{\text{H-Pt}}$ = 125.0 Hz), 4.77 (s, 1 H, H^a, $J_{\text{H-Pt}}$ = 72.0 Hz), 4.60 (br s, H^d) and 1.01 (s, 3 H, Me); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 150.0 (s, C^3), 148.2 (t, C^2, $J_{\text{C-P}}$ = 8.9 Hz), 135.5–128.0 (m, *Ph*$_3$P), 118.9 (s, C^1, $J_{\text{C-Pt}}$ = 62.3 Hz), 117.3 (br s, C^4), 19.6 (s, Me); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 24.9 (s, $J_{\text{P-Pt}}$ = 3228 Hz). Compound **3**: ^{1}H NMR (CD_2Cl_2, −30 °C) δ 7.51–7.13 (m, 30 H, *Ph*$_3$P), 6.01 (br d, 1 H, H^e, J_{ed} = 3.6 Hz), 5.47 (br d, 1 H, H^b, $J_{\text{H-P}}$ = 25.2 Hz), 5.06 (br d, 1 H, H^a, $J_{\text{H-P}}$ = 10.8 Hz), 4.97 (br s, 1 H, H^d), 1.33 (s, 3 H, Me); ^{13}C{^{1}H} (CD_2Cl_2, −30 °C) δ 164.8 (dd, C^2, $J_{\text{C-P}}$ = 110.3, 9.1 Hz), 149.6 (s, C^3), 134.8–129.7 (m, *Ph*$_3$P), 118.0 (s, C^1), 115.8 (br s, C^4), 20.7 (br s, Me). Compound **4**: ^{1}H NMR (CD_2Cl_2) δ 7.53–7.14 (m, 30 H, *Ph*$_3$P), 5.70 (dd, 1 H, H^d, $J_{\text{H-P}}$ = 16.5, $J_{\text{H-P}}$ = 7.2, $J_{\text{H-Pt}}$ = 4.2 Hz), 5.33 (br m, 1 H, H^c, $J_{\text{H-Pt}}$ = 64.8 Hz), 4.14 (dq, 1 H, H^b, J_{bc} = 10.0, $J_{\text{H-P}}$ = $J_{\text{H-P}}$ = J_{bc} = 3.2 Hz), 3.95 (br dd, 1 H, H^e, $J_{\text{H-P}}$ = 8.1, $J_{\text{H-P}}$ = 4.0 Hz), 3.23 (dd, 1 H, H^a, J_{ac} = 14.3, $J_{\text{H-P}}$ = 7.8, $J_{\text{H-Pt}}$ = 46.8 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 168.6 (d, C^3, $J_{\text{C-P}}$= 52.3 Hz), 134.7–129.0 (m, *Ph*$_3$P), 99.6 (C^4), 97.0 (C^2, $J_{\text{C-Pt}}$ = 16.0 Hz), 75.9 (d, C^1, $J_{\text{C-P}}$ = 23.5 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 21.6 (d, $J_{\text{P-P}}$ = 10, $J_{\text{P-Pt}}$ = 4267 Hz), 13.6 (d, $J_{\text{P-P}}$ = 10, $J_{\text{P-Pt}}$ = 3447 Hz), −144.4 (septet, PF_6^-). Compound **5**: ^{1}H NMR (CD_2Cl_2) δ 7.47–7.20 (m, 30 H, *Ph*$_3$P), 5.61 (ddd, 1 H, H^d, $J_{\text{H-P}}$ = 17.4, $J_{\text{H-P}}$ = 7.3, J_{de} = 3.2 Hz), 4.09 (br d, 1 H, H^b, $J_{\text{H-P}}$ = 10.5, $J_{\text{H-Pt}}$ = 37.5 Hz), 3.70 (br s, 1 H, H^e), 3.35 (br d, 1 H, H^a, $J_{\text{H-P}}$ = 7.4, $J_{\text{H-Pt}}$ = 32.4), 2.13 (s, 3 H, Me, $J_{\text{H-Pt}}$ = 66.4 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 168.2 (d, C^3, $J_{\text{C-P}}$ = 54.5 Hz), 134.7–129.0 (m, *Ph*$_3$P), 116.7 (C^2), 99.6 (C^4), 75.8 (d, C^1, $J_{\text{C-P}}$ = 24.2, $J_{\text{C-Pt}}$ = 75.0 Hz), 23.8 (s, Me, $J_{\text{C-Pt}}$ = 30.5 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 23.4 (d, $J_{\text{P-P}}$ = 11, $J_{\text{P-Pt}}$ = 4169 Hz), 15.8 (d, $J_{\text{P-P}}$ = 11, $J_{\text{P-Pt}}$ = 3287 Hz), −143.7 (septet, PF_6^-). Compound **6**: ^{1}H NMR (CD_2Cl_2) δ 7.47–7.06 (m, 45 H, *Ph*$_3$P), 5.95 (br s, 1 H, H^e), 5.40 (d, 1 H, H^b, $J_{\text{H-P}}$ = 19.4, $J_{\text{H-Pt}}$ = 108.0 Hz), 5.10 (d, 1 H, H^a, $J_{\text{H-P}}$ = 8.8, $J_{\text{H-Pt}}$ = 54.0 Hz), 4.73 (br s, 1 H, H^d), 0.70 (s, 3 H, Me); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 154.8 (dt, C^2, $J_{\text{C-P}}$ = 86.0, 10.9 Hz), 149.8 (br s, C^3), 135.6–127.8 (m, *Ph*$_3$P), 125.0 (br s, C^4), 120.0 (s, C^1, $J_{\text{C-Pt}}$ = 36.0 Hz), 21.2 (br d, *Me*, $J_{\text{C-P}}$ = 3.9 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 16.7 (d, $J_{\text{P-P}}$ = 19, $J_{\text{P-Pt}}$ = 2994 Hz), 14.4 (t, $J_{\text{P-P}}$ = 19, $J_{\text{P-Pt}}$ = 1725 Hz). Compound **8**: ^{1}H NMR (CD_2Cl_2) δ 7.65–7.36 (m, 30 H, *Ph*$_3$P), 5.76 (br d, 1 H, 1 H, H^e, J_{ed} = 2.9 Hz), 5.22 (s, 1 H, H^b, $J_{\text{H-Pt}}$ = 105.2 Hz), 4.70 (s, 1 H, H^a, $J_{\text{H-Pt}}$ = 59.4 Hz), 4.55 (br s, 1 H, H^c), 1.06 (s, 3 H, *Me*), −0.6 to −1.0 (br m, 3 H, B*H*$_3$CN); ^{13}C{^{1}H} NMR (C_6D_6) δ 149.9 (s, C^3), 144.9 (t, C^2, $J_{\text{C-P}}$ = 8.9 Hz), 135.1–128.5 (m, *Ph*$_3$P), 119.6 (s, C^1, $J_{\text{C-Pt}}$ = 59.4), 118.6 (s, C^4), 20.1 (*Me*) (BH_3*C*N not observed); ^{31}P{^{1}H} NMR (C_6D_6) δ 21.6 (s, $J_{\text{P-Pt}}$ = 3106 Hz); IR (KBr) ν(B–H) = 2336 (m), ν(CN) = 2200 (m) cm^{-1}. Compound **9**: ^{1}H NMR (C_6D_6) δ 7.69–6.81 (m, 30 H, *Ph*$_3$P), 5.94 (dd, 1 H, H$^{a/b}$, J = 21.4, 1.6, $J_{\text{H-Pt}}$ = 176.7 Hz), 4.56 (br d, 1 H, H$^{a/b}$, J = 8.1, $J_{\text{H-Pt}}$ = 110.0 Hz), 4.56 (s, 1 H, C*H*(CO_2Me)$_2$), 3.35 (s, 3 H, CO_2*Me*), 3.34 (s, 3 H, CO_2*Me*), 1.89 (br s, 3 H, *Me*), 1.66 (dt, 1 H, H$^{c/d}$, J_{cd} = 10.5 Hz), 0.95 (ddd, 1 H, H$^{c/d}$, J_{cd} = 10.5 Hz); ^{13}C{^{1}H} NMR (C_6D_6) δ 169.4 (*C*O_2Me), 169.3 (*C*O_2Me), 141.2 (d, C^2, $J_{\text{C-P}}$ = 105.0 Hz), 135.6–127.5 (m, *Ph*$_3$P), 112.5 (t, C^1, $J_{\text{C-P}}$ = 8.5 Hz), 62.7 (*C*H(CO_2Me)$_2$, $J_{\text{C-Pt}}$ = 38.5 Hz), 58.5 (dd, C^3, $J_{\text{C-P}}$ = 9.5, 3.5, $J_{\text{C-Pt}}$ = 54.7 Hz), 51.1 (CO_2*Me*), 27.5 (d, *Me*, $J_{\text{C-P}}$ = 3.5, $J_{\text{C-Pt}}$ = 53.5 Hz), 9.2 (d, C^4, $J_{\text{C-P}}$ = 75.0, $J_{\text{C-Pt}}$ = 437.5 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 25.9 (d, $J_{\text{P-P}}$ = 6, $J_{\text{P-Pt}}$ = 1878 Hz), 25.1 (d, $J_{\text{P-P}}$ = 6, $J_{\text{P-Pt}}$ = 1821 Hz). Compound **10**: ^{1}H NMR (C_6D_6) δ 7.80–6.80 (m, 30 H, *Ph*$_3$P), 4.10 (t, 1 H, *CH*, $J_{\text{H-H}}$ = 9.0 Hz), 3.32 (s, 6 H, CO_2*Me*), 2.32 (br m, 2 H, *CH*$_2$=C, $J_{\text{H-Pt}}$ = 60 Hz), 1.37 (t, 3 H, Me, J = 2.0 Hz) (the CH_2 resonances were observed as broad signals between δ 1.9–0.8); ^{31}P{^{1}H} NMR C_6D_6) δ 36.2 (d, $J_{\text{P-P}}$ = 40, $J_{\text{P-Pt}}$ = 3523 Hz), 28.1 (d, $J_{\text{P-P}}$ = 40, $J_{\text{P-Pt}}$ = 2986 Hz).

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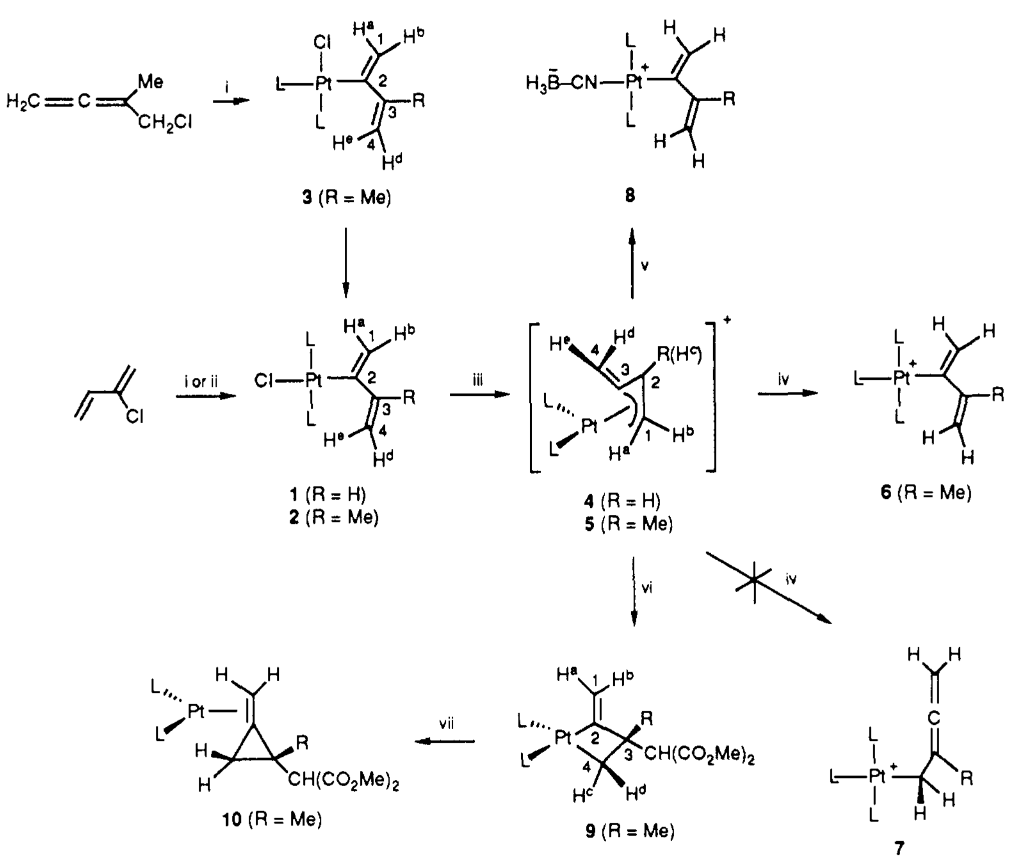
Scheme I[a]



[a] Legend: L = PPh_3; (i) $[Pt(C_2H_4)(PPh_3)_2]$ in THF, room temperature; (ii) $[Pt(C_2H_4)(PPh_3)_2]$ in $CHCl_3$, room temperature; (iii) $AgPF_6$ in CH_2Cl_2, room temperature; (iv) $+PPh_3$, THF; (v) $+Na[BH_3CN]$, THF; (vi) $KCH(CO_2Me)_2$, THF; (vii) Δ, C_6H_6.

product **2**. No other intermediates could be detected, and it seems likely that the formation of **3** arises via an η^2-allene complex, which subsequently undergoes a rapid intramolecular oxidative addition.

The molecules **1** and **2** are the first examples of 2-η^1-butadienyl complexes, and it was thought that a halide anion abstraction reaction would provide a rational route to cationic η^3-butadienyl complexes. Indeed, treatment of **1** and **2** with $AgPF_6$ in CH_2Cl_2 at room temperature led to the rapid precipitation of AgCl and formation of the yellow air-stable crystalline cationic complexes **4** (52%) and **5** (86%), characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.[8]

These cations are highly reactive, and treatment (2 h, room temperature) of, for example, **5** with triphenylphosphine led to attack on the platinum center and a reverse η^3 to η^1 transformation of the bonding mode of the butadienyl ligand. This gave the cation **6** in essentially quantitative yield, there being no evidence for the formation of the isomeric species **7**, containing a 1,2-diene ligand. Of greater potential interest were reactions involving delivery of a nucleophile to a carbon center of the η^3-butadienyl ligand; however, an attempt to achieve this by reaction (−78 °C and then warming to room temperature, THF) of **5** with $Na[BH_3CN]$ led surprisingly to the formation of **8**, where the $[BH_3CN]^-$ anion functions as an N-bonded ligand.[9] A wholly different result was obtained from the reaction of **5** with the soft carbon nucleophile $K[CH(CO_2Me)_2]$. Under mild conditions (3 h, room temperature, THF) this gave in high yield (82%) the colorless air-stable crystalline complex **9**. The most likely products of this reaction were thought to be a Pt(0) allene complex arising from nucleophilic attack on C_1 of the η^3-butadienyl ligand or a Pt(0) vinylcarbene species formed by attack on C_4. However, examination of the ^1H and $^{13}C\{^1H\}$ NMR spectra[8] showed that the cation **5** had undergone selective attack by the dimethyl malonate carbanion at C_2, i.e. the central allylic carbon, of the butadienyl ligand to form an *exo*-2-methyleneplatinacyclobutane. This is a surprising result, since nucleophilic attack at the central carbon of a η^3-allylic ligand is unusual;[10] moreover, the selective addition of nucleophiles to the terminal carbons of the allylic ligand present in the cations $[M(\eta^3\text{-allyl})(PPh_3)_2]^+$ (M = Pd, Pt) has been extensively documented.[11]

From a synthetic standpoint this anomalous result provides access to a rare[12] type of molecule containing a vinylidene-substituted metallacyclobutane. In an initial experiment directed to the exploration of the reactivity of these molecules, the thermolysis of **9** was examined. In refluxing benzene (5 h) a dark yellow solution was obtained, affording upon workup the yellow solid product **10**. Examination of the ^1H and $^{31}P\{^1H\}$ NMR spectra suggests[13] that **10** is a Pt(0) methylenecyclopropane complex as il-

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lustrated. The formation of a three-membered ring via a reductive-elimination reaction of this type is unusual,[14] compared with the reverse reaction, i.e. the oxidative insertion of metal fragments into strained three-membered rings.[15]

In summary, a new and potentially versatile route to η^3-butadienyl complexes has been described, which provides surprising[16] access to the relatively unexplored *exo*-vinylidenemetallacyclobutanes.

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(14) Athough there are examples of reductive-elimination reactions affording cyclopropanes (see: DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601), the formation of methylenecyclopropanes has not been reported.

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(16) It is hoped that a MO study of these cationic η^3-butadienyl complexes will provide an insight into the regioselectivity observed in this reaction.

Intramolecular C–X Activation as a Synthetic Route to Bidentate Cyclopentadienyl–Alkoxide Ligands: Preparation and Molecular Structure of (3-(2,3,4,5-Tetramethylcyclopentadienyl)propoxy)titanium Dichloride

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Summary: $Cp'TiCl_3$ (**1**; $Cp' = \eta^5\text{-}C_5Me_4(CH_2)_3OMe$) reacts with 2 equiv of the phosphorous ylide $PPh_3{=}CH_2$ (**2**) to yield $Cp'TiCl_2(CHPPh_3)$ (**3**) plus the phosphonium salt $(MePPh_3)Cl$. Complex **3** decomposes thermally to give $[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_3O]TiCl_2$ (**4**), containing a Cp*-alkoxide-functionalized ligand. The molecular structure of **4** shows it as a pseudo three-legged piano-stool complex.

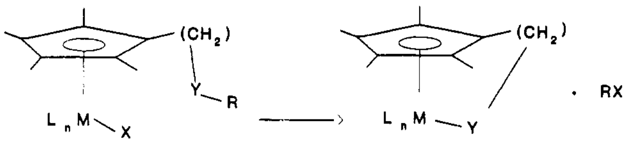
There is a rapidly growing interest in early-transition-metal and lanthanide compounds with bidentate ligands that combine two anionic functions, such as cyclopentadienyl ligands with built-in alkoxide, amide, or similar groups, in order to control their reactivity, e.g. as catalysts in the oligo- or polymerization of olefins. Several approaches have already been attempted,[1] but so far a systematic and convenient synthetic method has not been developed.

We decided to try a route based on the intramolecular thermally induced C–X activation of complexes containing a cyclopentadienyl ligand with a neutral basic function.

Here, we report the successful application of this approach to titanium, using a (tetramethyl(methoxypropyl)cyclopentadienyl)titanium ylide, $[\eta^5\text{-}C_5Me_4(CH_2)_3OMe]TiCl_2(CHPPh_3)$, as starting material. In metal ylides, $L_nMCHPPh_3$, the electronic charge on the ylidic carbon is intermediate between that of free ylides and coordinated ylides[2] so that they can act both as nucleophiles and as electrophiles. This versatility makes them very attractive for our synthetic purposes.

$Cp'TiCl_3$[3] (**1**; $Cp' = \eta^5\text{-}C_5Me_4(CH_2)_3OMe$) reacts instantaneously at room temperature with 2 equiv of CH_2PPh_3 (**2**) to give, through a transylidation process,[4] the titanium ylide $Cp'TiCl_2(CHPPh_3)$ (**3**) and the corresponding phosphonium salt in an essentially quantitative yield (eq 1).

Scheme I



$$\underset{\mathbf{1}}{Cp'TiCl_3} + \underset{\mathbf{2}}{CH_2{=}PPh_3} \rightarrow [Cp'TiCl_3(CH_2PPh_3)] \xrightarrow[-PPh_3MeCl]{+2} \underset{\mathbf{3}}{Cp'TiCl_2(CHPPh_3)} \qquad (1)$$

Ylide **3** is the only titanium product formed. When the reaction is carried out with lower ylide:titanium ratios, the ylide is consumed to produce **3** according to eq 2 and the excess **1** is found unchanged. The mechanism of this reaction has not been studied, but intermediate formation of an ylide adduct, which transfers a proton to the free ylide, followed by extrusion of a chloride ligand seems quite plausible.[5]

Compound **3** is extremely air-sensitive but thermally rather stable. It is very soluble in toluene and ethers but only poorly soluble in alkane solvents.

The bond in the titanium ylide can be represented as being composed of forms A and B.

$$\underset{\text{A}}{Ti{-}C^{-}H{-}P^{+}Ph_3} \qquad \underset{\text{B}}{Ti^{-}{=}CH{-}P^{+}Ph_3}$$

^1H and ^{13}C NMR spectroscopy[6] points to a large con-

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