$(CH_2C_6H_4CH_3)(CNBu\text{-}t)_4$, 98170-47-9; $Mg(o\text{-}CH_3C_6H_4CH_2)Cl$, 29875-05-6; $Ni(cod)_2$, 1295-35-8; $o\text{-}ClCH_2C_6H_4Me$, 552-45-4; $NaS_2CN(Me)_2$, 128-04-1; $NaS_2CN(i\text{-}Pr)_2$, 4092-82-4; *t*-BuNC, 7188-38-7; 1,2-bis(2-methylphenyl)ethane, 952-80-7.

**Supplementary Material Available:** Tables of fractional coordinates of atoms, thermal parameters, and observed and calculated structure factors for **3** (25 pages). Ordering information is given in any current masthead page.

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# A Novel Transition-Metal-Promoted Rearrangement of a Cyclopropenyl Cation. Synthesis and Crystal and Molecular Structure of a 1-3-$\eta$-Butadienyl Complex of Platinum

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*Summary:* Reaction of the methyldiphenylcyclopropenyl cation (**2**) with bis(triphenylphosphine)(ethylene)platinum(0) (**3**) affords the (1-3-$\eta$-butadienyl)platinum complex **6**, via an unprecedented ring-opening reaction coupled with a hydrogen shift. The crystal and molecular structure of **6** has been determined.

Reactions of cyclopropenyl cations with transition-metal complexes have afforded a diverse array of organometallic compounds. In addition to simple 3-$\eta^1$- and $\eta^3$-cyclopropenyl complexes, a number of other interesting and useful ligands have been derived from ring-opening or ring expansion reactions of these versatile three-membered organic rings.[3] An unusual mode of coordination for the intact triphenylcyclopropenyl ligand is found in its cationic complexes **1** containing the $ML_2$ fragment (M = Ni, Pd, Pt; L = $PPh_3$).[4,5] In these compounds the cyclopropenyl ring adopts a coordination mode perhaps best described as $\eta^2$, as evidenced by crystallographic determinations on compounds of all three metals of the nickel triad. These $\eta^2$-cyclopropenyl compounds are fluxional in solution, exhibiting a low-energy "ring-whizzing" of the $ML_2$ fragment. The pathway by which the metal perambulates around the periphery of the ring has been examined theoretically, and various points along this pathway are defined by the different conformational relationships between the $ML_2$ fragment and the cyclopropenyl ring which are observed in the solid-state structures of **1**.[4]

We now report that this mode of coordination does not always result in isolable cyclopropenyl complexes and that when a methyl group is present on the three-membered ring, a novel skeletal rearrangement coupled with a hydrogen shift can occur to give the 1-3-$\eta$-butadienyl ligand, further extending the range of ligand types available from cyclopropenyl cation precursors.

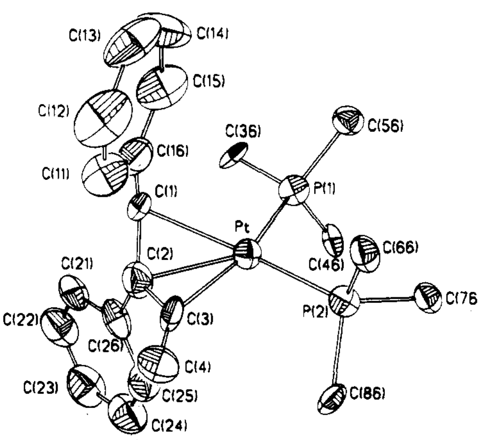
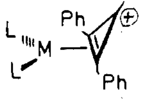
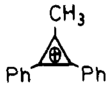


**Figure 1.** The molecular geometry and labeling scheme for **6**, drawn with 40% probability ellipsoids. Only the ipso carbon atoms of the phenyl groups of the triphenylphosphine ligands are shown. Selected bond lengths (Å): Pt–P(1), 2.339 (4); Pt–P(2), 2.289 (4); Pt–C(1), 2.291 (14); Pt–C(2), 2.201 (14); Pt–C(3), 2.075 (13); C(1)–C(2), 1.40 (2); C(2)–C(3), 1.46 (2); C(3)–C(4), 1.31 (2); Selected bond angles (deg): P(1)–Pt–C(1), 97.3 (4); P(1)–Pt–C(2), 120.3 (4); P(1)–Pt–C(3), 159.9 (4); P(2)–Pt–C(1), 155.0 (4); P(2)–Pt–C(2), 134.3 (4); P(2)–Pt–C(3), 95.7 (4); C(1)–Pt–C(2), 36.2 (5); C(1)–Pt–C(3), 66.9 (5); C(2)–Pt–C(3), 39.7 (6); C(1)–C(2)–C(3), 115 (1); C(2)–C(3)–C(4), 140 (1); P(1)–Pt–P(2), 103.0 (1).

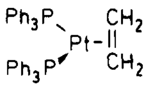
By analogy with the previously documented reaction of the triphenylcyclopropenyl cation,[5] it was anticipated that reaction of **2** with the platinum(0) complex **3** should afford the $\eta^2$-cyclopropenyl complex **4**. It was envisaged that subsequent deprotonation of **4** would lead to the $\eta^2$-methylenecyclopropene compound **5**, thus providing the first example of a transition-metal complex of this smallest cross-conjugated fulvene skeleton.[6] Contrary to these expectations, addition of an equimolar amount of tetrafluoroborate salt of **2** to a $CH_2Cl_2$ solution of **3** resulted in a sudden color change from pale yellow to bright orange, with subsequent rapid fading to a golden yellow color. Workup afforded high yields of a bright yellow crystalline solid, **6**.[7] While microanalysis results indicated that this



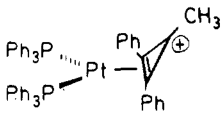
**1**



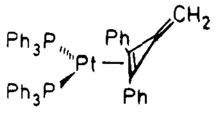
**2**



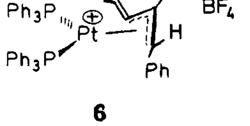
**3**



**4**



**5**



**6**

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(1) (a) Dartmouth College. (b) University of Delaware.

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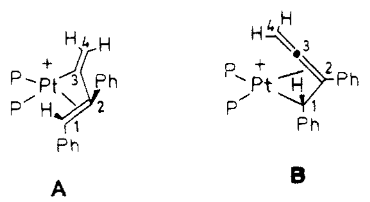


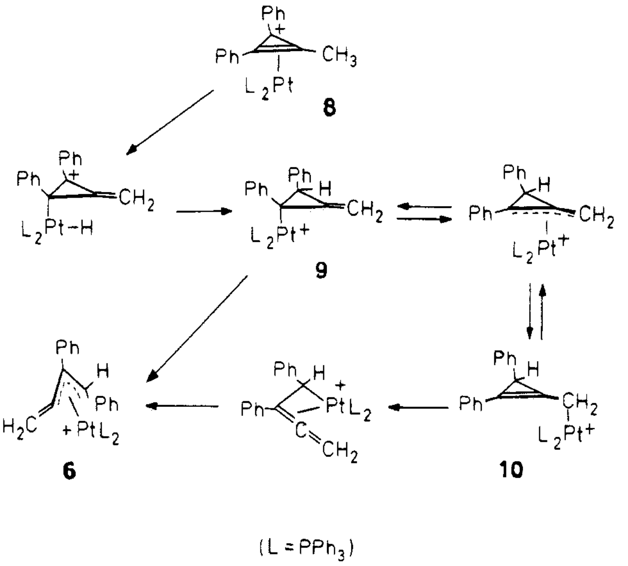
**Figure 2.** Valence bond representations of the metal-carbon bonding in complex 6.

material had the elemental composition expected for the ionic compound 4, both $^1H$ and $^{13}C$ NMR studies failed to show resonances characteristic of a methyl group. However the $^1H$ NMR spectrum ($CDCl_3$ solution) did exhibit phenyl resonances (relative intensity = 10 protons) together with two unit intensity resonances at low field ($\delta$ 6.03 and 6.12), characteristic of protons on an uncoordinated olefin, and a third, higher field resonance at $\delta$ 4.64, also of unit intensity; the $^{31}P$ NMR spectrum demonstrated inequivalent phosphine ligands. These data seemed consistent with the illustrated structure 6, which contains an extremely rare example of a 1–3-$\eta$-butadienyl ligand.

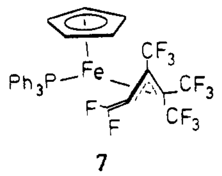
In view of the rarity of this class of ligand, compound 6 was subjected to a single-crystal X-ray diffraction study. Figure 1 illustrates the molecular structure of 6, together with selected bond distances and angles.[8] Fractional atomic coordinates for 6 and complete listings of bond lengths, bond angles, temperature factors, and observed and calculated structure factors are provided as supplementary material.[9]

The overall geometry of 6 clearly defines the structural features of the 1–3-$\eta$-butadienyl ligand. The two most reasonable valence bond representations for metal–carbon interactions in this compound are illustrated as A and B in Figure 2. The Pt–C(3) distance [2.075 (13) Å] is significantly shorter than the Pt distances to C(1) [2.291 (14) Å] or C(2) [2.201 (14) Å], and the Pt–P(1) distance [2.339 (4) Å] is significantly longer than the Pt–P(2) distance [2.289 (4) Å]; both observations support the idea that the Pt–C(3) interaction is more of a $\sigma$-bond in character, with a correspondingly higher trans influence. The C(1)–C(2) distance [1.40 (2) Å] is slightly shorter than the C(2)–C(3) distance [1.46 (2) Å], though both are significantly longer than the uncoordinated C(3)–C(4) separation of 1.31 (2) Å, and the two phenyl rings occupy mutally trans positions with respect to the C(1)–C(2) bond. We conclude that the metal-carbon bonding in 6 is best represented as a hybrid of A and B, with A being the dominant contributor.

**Scheme I**



This class of ligand is indeed rare. Although one report of two Fe and Mo complexes containing similar ligands has recently appeared,[10] the only other structurally characterized complex containing a 1–3-$\eta$-butadienyl ligand appears to be the iron–fluorocarbon derivative 7;[11] none of these complexes was obtained from a three-membered ring precursor.



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The mechanism of formation of 6 is unclear, but two possible pathways are illustrated in Scheme I. Initial formation of $\eta^2$-cyclopropenyl species 8, isomeric with 4, accesses an intermediate which can undergo metal-assisted H transfer as shown to give the $\eta^1$-allylic complex 9. This is a coordinately unsaturated cyclopropyl–Pt species which can undergo ring opening to afford the final product 6. Similar ring-opening reactions to give $\eta^3$-allyl ligands have been observed for coordinatively unsaturated cationic cyclopropyl–Pt compounds.[12] Alternatively, $\eta^1$ to $\eta^3$ to $\eta^1$ isomerization of 9 would afford 10, which might be expected to undergo ring cleavage as shown to give 6. The C–C bond breaking step in this latter reaction is analogous to that previously postulated for coordinatively unsaturated cyclopropylcarbinyl palladium[13] and platinum[12,14] species.

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(7) Compound **6**: 85%, decomp pt 156–160 °C; $^1H$ NMR (300 MHz, 20 °C, $CDCl_3$) $\delta$ 6.92–7.66 (10 H, Ph), 6.12 [1 H, *J*(P–H) = 20, 9 Hz, J(H–H) = 2.5 Hz, *J*(Pt–H) = 40 Hz, C=C*H*$_2$], 6.03 [1 H, *J*(P–H) = 5, 2.5 Hz, *J*(H–H) = 2.5 Hz, *J*(Pt–H) = 36 Hz, C=C*H*$_2$], 4.64 [1 H, *J*(P–H) = 10, 2.5 Hz, *J*(Pt–H) = 20 Hz, C*H*Ph]; $^{31}P$ NMR ($CDCl_3$; ppm upfield from $H_3PO_4$) $\delta$ 13.8 [*J*(Pt–P) = 2118 Hz, *J*(P–P) = 9 Hz], 27.3 [*J*(Pt–P) = 1640 Hz, *J*(P–P) = 9 Hz]. Anal. Calcd for $C_{52}H_{43}BF_4P_2Pt$: C, 61.73; H, 4.28; P, 6.12. Found: C, 61.53; H, 4.20; P, 6.11.

(8) Crystal data (22 °C): orthorhombic, space group *Pbca*, $a = 21.840$ (4) Å, $b = 21.732$ (5) Å, $c = 18.680$ (2) Å, $V = 8866.2$ (32) Å$^3$, $Z = 8$. Of 5563 unique reflections collected on a Nicolet R3 diffractometer, 3416 were considered observed at the $F > 3\ \sigma(F)$ level. The structure was solved by heavy-atom methods and subsequent difference Fourier syntheses, using a crystal of dimensions 0.07 × 0.33 × 0.36 mm. An empirical absorption correction based upon a lamina model (major crystal face [010] with rejection of data with a glancing angle of ≤3° was applied to all data. This resulted in the elimination of 354 reflections strongly affected by knife-edge effects. All non-hydrogen atoms were refined with anisotropic thermal parameters. Phenyl rings were treated as rigid bodies (C–C = 1.395 Å). Despite the $BF_4^-$ anion's constraint to a rigid tetrahedron with a refined B–F distance (1.29 (1) Å), high thermal parameters associated with it suggest that some disorder exists; however, no peaks in the final difference map associated with the $BF_4^-$ were found with an electron density greater than 0.4 e Å$^{-3}$. At convergence $R_F = 0.63$, $R_{wF} = 0.058$, and GOF = 1.255. All computer programs are contained in the SHELXTL (4.1) program library (G. Sheldrick as distributed by the Nicolet Corp., Madison, Wi). Fractional atomic coordinates, bond distances and angles, and additional crystallographic data are available as supplementary material.[9]

(9) See paragraph at end of text regarding supplementary material.

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Experiments are in progress to explore the scope of this reaction, the chemistry of **6** and its relatives, and to determine whether the ring-opening/hydrogen shift process is indeed intramolecular in nature.

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**Registry No.** **2**·$BF_4$, 65102-02-5; **3**, 12120-15-9; **6**, 98539-85-6.

**Supplementary Material Available:** Tables of atomic coordinates and isotropic temperature factors for non-hydrogen atoms (Table 1S), bond lengths (Table 2S), bond angles (Table 3S), anisotropic temperature factors (Table 4S), and observed and calculated structure factor tables (Table 5S) (25 pages). Ordering information is given on any current masthead page.

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# Indenylmolybdenum Dicarbonyl and Indenylmolybdenum Tricarbonyl Dimers: A Clarification of Their Syntheses and Spectroscopic Characteristics, Including the Structure of the Previously Unrecognized Triply Bonded Species

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*Summary:* The reaction of indene with molybdenum hexacarbonyl in diglyme/octane at 165 °C generates indenylmolybdenum dicarbonyl dimer directly rather than the tricarbonyl dimer as had been previously reported. Spectroscopic characteristics of the dicarbonyl dimer as well as its single-crystal X-ray structure are presented. The indenyl ligands are bound in $\eta^5$ fashion, and the metal–metal distance is in the expected range for a Mo–Mo triple bond. The complex reacts readily with carbon monoxide to form the known tricarbonyl dimer.

The reactivity of the triple bond in $[CpMo(CO)_2]_2$ has been widely studied since this fascinating complex was first prepared.[1] It's high reactivity makes the dimer a useful starting material in the preparation of a variety of clusters. Synthesis of the indenyl analogue would be particularly interesting, because of possible heightened reactivity at the molybdenum centers due to the "indenyl effect"[2] and because of the use of the indenyl complex as a precursor to other clusters in which the "indenyl effect" might be studied.

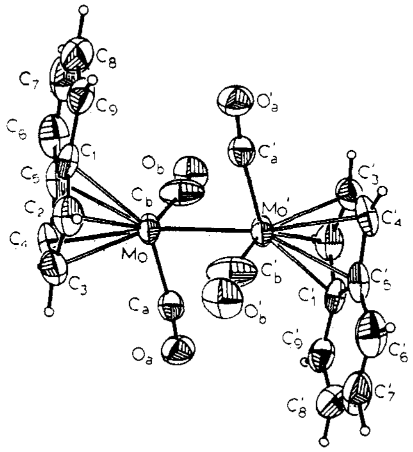

**Figure 1.** X-ray crystal structure of $[Mo(C_9H_7)(CO)_2]_2$, **1**. Selected interatomic distances (Å) and bond angles (deg): Mo–Mo' = 2.500 (1), Mo–$C_a$ = 1.953 (7), Mo–$C_b$ = 2.098 (9), Mo–$C_a'$ = 2.753 (7), Mo–$C_b'$ = 2.692 (9), $O_a$–$C_a$ = 1.155 (9), $O_b$–$C_b$ = 1.107 (10), Mo–$C_1$ = 2.401 (6), Mo–$C_2$ = 2.332 (7), Mo–$C_3$ = 2.336 (7), Mo–$C_4$ = 2.348 (7), Mo–$C_5$ = 2.396 (7); $C_a$–Mo–Mo' = 75.3 (2), $C_b$–Mo–Mo' = 71.1 (3), Mo–$C_a$–O = 173.6 (5), Mo–$C_b$–O = 171.2 (8).

**Table I. Infrared Carbonyl Stretching Frequencies and UV-Vis Band Maxima for $[Mo(C_9H_7)(CO)_2]_2$, 1, $[Mo(C_9H_7)(CO)_3]_2$, 2, and Their Cyclopentadienyl Analogues[a]**

| compound | IR, $cm^{-1}$ | UV-vis, nm |
|---|---|---|
| $[Mo(C_9H_7)(CO)_2]_2$, 1 | 1893 (s), 1858 (s) | 349 |
| $[Mo(C_5H_5)(CO)_2]_2$ | 1895 (s), 1855 (s) | 322, 380 (sh) |
| $[Mo(C_9H_7)(CO)_3]_2$, 2 | 2020 (w), 1958 (s), 1910 (s) | 410, 510 |
| $[Mo(C_5H_5)(CO)_3]_2$ | 2020 (w), 1959 (s), 1913 (s) | 382, 507 |

[a] All spectra run in $CH_2Cl_2$ solvent under inert atmosphere.

A logical approach to the synthesis of the previously unreported triply bonded dimer $[IndMo(CO)_2]_2$, **1**, appeared to be through the singly bonded dimer $[IndMo(CO)_3]_2$, **2**, which had been reported by several authors to be accessible via the direct reaction of $Mo(CO)_6$ with indene in high boiling solvents.[3-5] We have found that under one such set of conditions the triply bonded dimer **1** is produced directly and in fact suspect that the material previously characterized as the singly bonded dimer **2** was,

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