Carbon–Carbon and Carbon–Oxygen Bond Formation from the Reaction of Platinum(II) with Bicyclo[4.1.0]hept-2-ene and Related Derivatives

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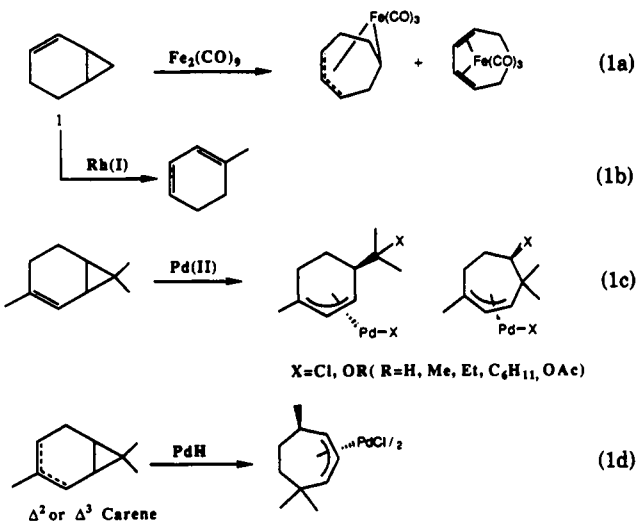
Bicyclo[4.1.0]hept-2-ene is readily transformed stereospecifically and regiospecifically via Pt(II) to trans-disubstituted cyclohexane and cyclohexene derivatives. A Pt(II) intermediate has been isolated.

Introduction

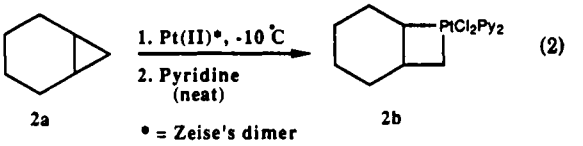
Transition metal facilitated organic transformations have shown promise and have received considerable attention over the last few years. In this article, we wish to reinforce the above concept by elaborating on the reaction between platinum(II) and bicyclo[4.1.0]hept-2-ene (1) (norcarene).

Success in the past with the above-mentioned bicyclic system has been somewhat limited. Aumann[1] studied its reaction with $Fe_2(CO)_9$ in which the formation of the stable η^4-diene complex occurred (eq 1a). He also proposed and



isolated the π-allylic intermediate shown. Other transition metals that have been reacted with 1 include Rh, Ti, Cr, Ni, and Pd. Of these, rhodium[2] was found to catalyze its isomerization to 1-methyl-1,3-cyclohexadiene at 75 °C (eq 1b). Further, Pd(II) was allowed to react with the analog, Δ^2-carene, to yield trans X-palladation in both six- and seven-membered ring systems (eq 1c).[3] Finally, either Δ^2- and Δ^3-carene was allowed to react with palladium hydride as shown in eq 1d.[4] As will be seen below, the reaction of norcarene with Pt(II) proceeds by a route entirely different from those briefly discussed above. The remaining metals did not cause any change in 1 leading to the conclusion that metal insertion had not occurred.[5]

Although the chemistry of 1 with transition metals has been limited as noted above, the possibility of its reaction with platinum and subsequent elaborations was excellent. For example, previous results in this laboratory had shown that bicyclo[4.1.0]heptane reacted with Pt(II) to form a metallacyclobutane[6] (eq 2). Since **2b** is relatively unstable

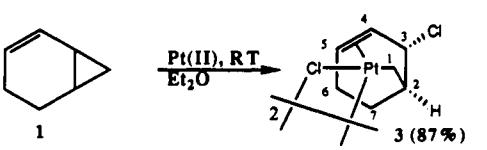


tending to react from a C^+--Pt^- σ-bond polarization, we anticipated that the reaction of Pt(II) with 1 would yield the π-allylic intermediate I which would be different from

that proposed in Aumann's work. One would then expect nucleophilic attack at either of the cationic sites. Moreover, the nucleophile could come from either face of the cyclohexyl ring possibly yielding a mixture of four isomers. However, models and modeling studies of this intermediate suggested that the platinum(II) moiety of I is not symmetrically disposed with regard to the π-allylic system and is better viewed as structure II. Thus, an unequal mixture was anticipated.

Results and Discussion

Reaction of 1 with Pt(II). The reaction result, shown as eq 3, not only indicates that the reaction proceeds as



anticipated and is different from all previous work but also that it is regiospecific with nucleophilic substitution only at C-3. Moreover, it is stereospecific with the nucleophile bonding trans to the platinum moiety. Finally, the platinum atom has emerged from the reaction as a Pt(II) unit as anticipated and will be useful for additional functionalization (vide infra).

Evidence for the structure of complex **3** is derived from its ^1H, ^{13}C, and ^{195}Pt NMR spectra and elemental analysis. The key NMR features are as follows: a platinum reso-

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(3) (a) Backvall, Jan-E.; Bjorkman, E. E. *J. Chem. Soc., Chem. Commun.* **1982**, 693. (b) Wilhelm, D.; Backvall, Jan-E.; Nordberg, R. E.; Norin, T. *Organometallics* **1985**, *4*, 1296.
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(5) Gladysz, J. A.; Fulcher, J. G.; Ugolick, R. C.; Hanlan, A. J. L.; Bocarsly, A. B. *J. Am. Chem. Soc.* **1979**, *101*, 3388.
(6) Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 3973.

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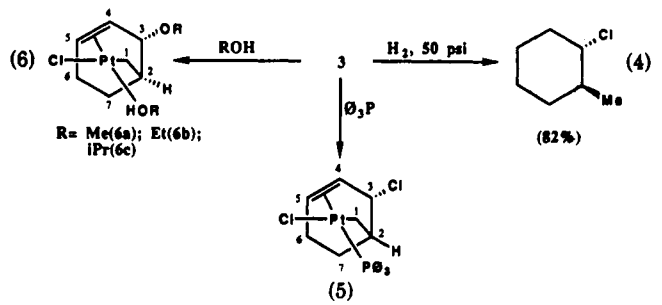
Table I. ^{13}C NMR Data for Complexes 3, 5, and 10[a]

no.	3	5	10
1	13.9 (618.6)	13.5 (625.6) ($J_{P,C}$ = 0)	4.5 (577.7)
2	35.5 (<10)	36.9 (37.3)	27.3 (27.9)
3	58.3 (82.0)	57.0 (64.4)	72.9 (40.7)
4[b]	80.5 (248.3)	104.7 (96.6) ($J_{P,C}$ = 13.8)	53.9 (377.2)
5[b]	80.8 (248.3)	110.6 (86.6) ($J_{P,C}$ = 10.9)	57.2 (341.8)
6	20.4 (38.8)	22.6 (25.4)	20.0 (unres)
7	20.3 (0)	20.1 (0)	20.0 (0)
8			

[a] Relative to $CDCl_3$. $J_{Pt,C}$ values in Hz are in parentheses. [b] Not rigorously assigned.

nance at 1250 ppm downfield of the standard $Na_2Pt(CN)_4$ suggesting a Pt(II) moiety;[7] strong platinum coupling (618 Hz)[8] to a single carbon, C(1), and platinum coupling to the olefinic resonances which are shifted upfield to 80.5 and 80.8 ppm ($J_{Pt,C}$ = 248);[9] a single carbon resonance downfield at 58 ppm assigned to C(3) which bears an electronegative substituent, presumably chlorine. Table I lists the ^{13}C NMR data for complex 3.

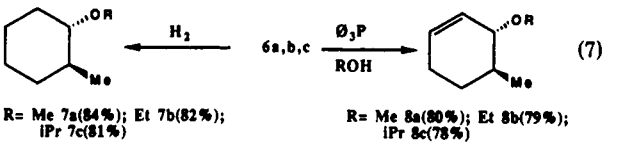
Further evidence for the structure of 3 was obtained from the facile release of the organic moiety (eq 4). The



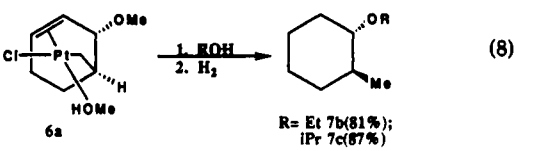
^1H NMR data for product 4 are identical to that reported in the literature including the $^3J_{H,H}$ coupling constant of 11.0 Hz,[10] which establishes the stereo- and regiochemistry of the substituents. While this does not directly establish the stereochemistry of 3, it suggests that the proposed structure is likely. Subsequent results from other reactions, vide infra, will also support the structure proposed. Finally, the double-bond location in 3 was garnered from COSY and HETCOR NMR experiments.

Reactions of Complex 3. Triphenylphosphine. On reaction with Ph_3P, the dimeric nature of 3 is lost (eq 5). NMR analysis of 5 shows that the phosphine is trans to the olefin as evidenced by its coupling of 10.9 and 13.8 Hz to the olefinic carbons versus 0.0 Hz to the Pt–CH_2 moiety. Carbon NMR data for 5 are consistent with its proposed structure and are listed in Table I.

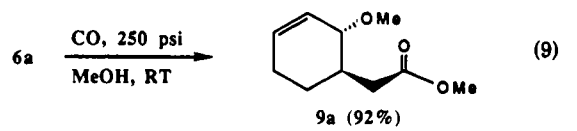
Alcohols. Reaction of 3 with alcohols to form 6a–c indicates the potentially rich chemistry that this system possesses (eq 6). That is, the platinum moiety not only facilitates substitution of the chlorine functionality but also directs the incoming nucleophile so that the regio- and stereochemistry of the original complex 3 is retained. Subsequent hydrogenation of the alkoxy derivatives 6a–c leads to compounds 7a–c, which again have the 1,2-trans stereochemistry (eq 7).[11] Equally significant is the reaction



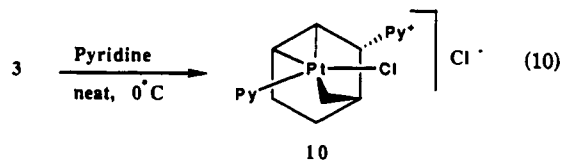
of 6a–c with Ph_3P in alcohol, which not only releases the organic moiety from the metal while retaining the 1,2-trans stereochemistry[12] but also preserves the olefinic functionality (eq 7). Thus, complex 3 or 6 with its π-complexed platinum moiety appears to have the excellent feature which allows one to replace the electronegative substituent at C-3 with another nucleophile while retaining both stereo- and regiochemistry. Moreover, if one wishes to change the alkoxy functionality, it merely requires refluxing of 6a with the desired alcohol and subsequent reaction with H_2 to liberate the organic moiety (eq 8).



Carbon Monoxide. The question of whether the Pt–CH_2 bond of complex 3 could be further functionalized through the use of carbon monoxide was addressed. Treatment of 6a under relatively mild conditions[13,14] produced 9a in excellent yields (eq 9). This reaction occurs readily at temperatures of 10–15 °C and at a relatively low pressure of 250–300 psi. Under higher temperatures the allylic isomers of 9a are produced.



Pyridine. Reaction of 3 with pyridine provides the unique result shown in eq 10. Evidence for complex 10



comes from comparison of its NMR data to that of complex 5 (Table I). As can be seen, the resonances for C-4 and C-5 in complex 10 have shifted upfield by some 50 ppm compared to those for complex 5. In addition, the Pt–C coupling constants to C-4 and C-5 have increased by

(7) Pt(IV) complexes are found at 2500–3400 ppm whereas Pt(II) complexes range from 680 to 1600 ppm relative to $Na_2Pt(CN)_4$. (a) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (b) Ekeland, R. A.; Jennings, P. W. *J. Organomet. Chem.* **1985**, *281*, 397. (c) Waddington, M. D. Ph.D. Dissertation, Montana State University, 1984.

(8) Pt–C σ-bond coupling in unstrained systems usually ranges from 550 to 800 Hz. (a) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 439. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1253. (c) Waddington, M. D.; Campbell, J. A.; Jennings, P. W. *Organometallics* **1983**, *2*, 1269. (d) Burton, J. T.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1312.

(9) Platinum–olefin coupling normally ranges from 100 to 250 Hz. (a) Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 1793. (b) Hoberg, J. O.; Larsen, R. D.; Jennings, P. W. *Organometallics* **1990**, *9*, 1334.

(10) Monnier, M.; Aycard, J. P. *Can. J. Chem.* **1979**, *57*, 1257.

(11) Compound 7a and its stereochemistry were confirmed by comparison to the known trans ether, synthesized from reaction of the pure trans alcohol (Aldrich) with MeI and NaH, and also by comparison of ^{13}C NMR data to: Haines, et al. *J. Chem. Soc., Perkin Trans.* **1981**, *1*, 1671.

(12) Stereochemistry was assigned by comparison with similar compounds reported in: Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655.

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(14) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306, 1310; **1977**, 1892. Brune, H. A.; Falck, M.; Hemmer, R.; Ait, H. G. *Chem. Ber.* **1984**, *117*, 2803. Brune, H. A.; Hess, R.; Schmidtberg, G. *Chem. Ber.* **1985**, *118*, 2011. Hackett, M.; Whitesides, G. M. *Organometallics* **1987**, *6*, 403.

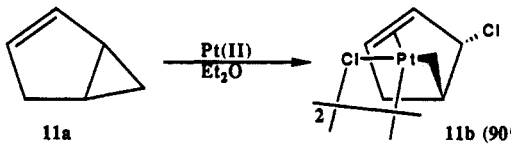
Table II. ^{13}C NMR Data for Complexes 11b[a] and 12b

no.	11b	12b
1	25.6 (671.4)	13.1 (628.0)
2	44.5 (<10)	41.6 (<10)
3	64.9 (61.0)	64.6 (93.2)
4	83.0[b] (305.2)	82.8[b] (249.0)
5	87.3[a] (300.6)	82.8[b] (249.0)
6	38.7 (0)	28.9 (20)
7		26.8 (0)
8		23.0 (30.5)

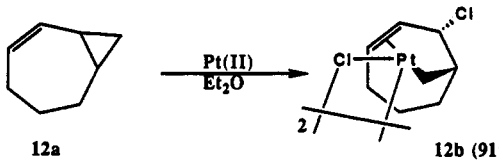
[a] Relative to $CDCl_3$. $J_{Pt,C}$ values in Hz are in parentheses. [b] Not rigorously assigned.

100 Hz suggesting stronger bonding. As a result, we are suggesting that the platinum olefin moiety is better described as a platinacyclopropane rather than as a simple π-bound olefin. Precedence for this type of platinacyclopropane moiety also comes from comparison to literature data.[15] Carbon C-3 is shifted downfield by 26 Hz either as a result of the platinacyclopropane perturbation or because the chlorine has been substituted by pyridine as shown. Finally, ^{195}Pt NMR spectroscopy of **10** suggests that the platinum has been oxidized toward the +4 oxidation state with a resonance at 1890 ppm. This is compared to the platinum resonance in complex **5** which occurs at 680 ppm and complex **3** where it resonates at 1253 ppm. Platinum(II) complexes generally resonate near 1000 ppm, and Pt(IV) complexes are found in the 2500–3400 ppm range.[7]

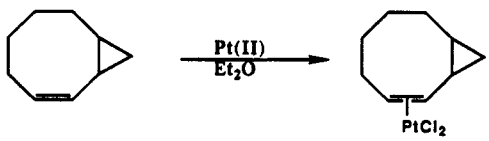
Additional Substrates. With the excellent results derived from compound **1**, use of other vinylcyclopropane derivatives was attempted. Equations 11–13 show the



11a 11b (90%) (11)



12a 12b (91%) (12)



13a 13b (13)

results. Complexes **11b** and **12b** were readily formed as white solid materials in excellent yields. Comparison of the NMR data for those with complex **3** showed excellent correlation (Table II). Reaction of compound **13a** with Pt(II), however, resulted only in the formation of the orange solid π-complex **13b**. Attempts at insertion, including the use of elevated temperatures and excess platinum, have not yielded platinum reaction with the cyclopropyl moiety.

Summary

The successfully completed reactions of bicyclo[4.1.0]-hept-2-ene and homologues with Pt(II) represent an example of extensive stereo- and regiochemical control in the elaboration of norcarene chemistry. Moreover, the Pt(II)-facilitated substitution of allylic ethers with regio- and stereospecific control is novel in platinum chemistry. Finally, the methodology for carbonylation of Pt(II) derivatives under relatively mild conditions is a significant advance.

Experimental Section

General Methods. ^1H NMR spectra were obtained on Bruker AM 500, AC 300, or WM 250 MHz instruments. Chemical shifts are reported in units of parts per million (ppm) with ^1H NMR shifts relative to solvents. ^{13}C NMR spectra were recorded at 125.76, 75.5, or 62.9 MHz, and chemical shifts are reported relative to the solvent resonance. $^{195}Pt\{^1H\}$ NMR spectra were recorded at 53.66 MHz, and chemical shifts are given relative to external 1 M $Na_2Pt(CN)_4$. $^{31}P\{^1H\}$ NMR spectra were recorded at 101.27 MHz, and chemical shifts are given relative to external 85% H_3PO_4. All coupling constants are reported in hertz. All complexes and organic products were assigned using both 1- and 2-dimensional NMR techniques. Mass spectral data were collected on VG MM-16 and 7070 spectrometers. Infrared spectra were obtained on a Nicolet SDX FT-IR spectrometer. Preparative GC collections were made with a Varian 3300 FID equipped with a 10 ft × $^1/_4$ in. column packed with SE 30 on Chromsorb W. Elemental analyses were done by Galbraith Laboratories. High-pressure reactions were run in a Parr Instrumental Bomb No. 4702, type T304SS with glass insert.

Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used without further purification. Diethyl ether was distilled from sodium benzophenone. Chloroform was washed with water five times, distilled from $CaCl_2$, and stored in the dark over 4-Å molecular sieves. Pentane was distilled from $LiAlH_4$. Zeise's dimer was prepared from K_2PtCl_4 which was a loan from Johnson-Matthey Corp. Synthesis of cyclopropanes are reported as improved procedures over literature procedures.[16] Additionally, updated data for cyclopropanes are reported.[17]

Formation of 1. A 3-mL volume (31.5 mmol) of 1,3-cyclohexadiene at −10 °C was reacted with CH_2N_2 in dry ether in the presence of a catalytic amount of $PdCl_2$ for 3 h. The CH_2N_2 was generated by addition of 15 g of Aldrich diazald to 2 g of KOH in 5 mL of water and 12 mL of 2-(2-ethoxyethoxy)ethanol as a solvent. The mixture was allowed to stir 12 h and then filtered. Distillation afforded 1.8 g of **1** (61% yield): ^1H NMR ($CDCl_3$) 5.95–6.05 (m, 1 H), 5.3–5.4 (m, 1 H), 1.9–2.0 (m, 2 H), 1.65–1.80 (m, 1 H), 1.5–1.62 (m, 1 H), 1.2–1.32 (m, 1 H), 1.1–1.2 (m, 1 H), 0.65–0.75 (ddd, 1 H), 0.55–0.62 (ddd, 1 H); ^{13}C NMR ($CDCl_3$) 128.87 (d), 122.75 (d), 20.68 (t), 18.58 (t), 13.89 (d), 10.06 (t), 9.71 (d); ms *m/e* (%) 94 (M^+, 44.5), 91 (16.6), 79 (100), 77 (36.9), 66 (17). It is a known compound.

Reaction of 1 with Pt(II). In a 5-dram vial was placed 25.5 μL (23.3 mg, 0.24 mmol) of **1** and 4 mL of dry diethyl ether. Zeise's dimer (72 mg, 0.12 mmol) was added, and the mixture was stirred at room temperature for 1 h to yield a white precipitate. The precipitate was washed one time with 6 mL of pentane and dried under vacuum yielding 156 mg of **3** in 87% yield. Anal. Calcd for $C_{14}H_{20}Cl_4Pt_2$: C, 23.33; H, 2.77. Found: C, 22.98; H, 2.71. IR (KBr): 868.0, 816.7, 786.0, 734.7, 560.4 (s). ^1H NMR ($CDCl_3$): 4.78 (m, $J_{Pt,H}$ = 81.64, H-5), 4.42 (dd, $J_{Pt,H}$ = 95.2, H-4), 4.46 (dd, $J_{H,H}$ = 3.81, H-3), 2.6–2.7 (m, H-6), 2.46–2.55 (m, H-6), 2.22–2.31 (m, H-7), 2.05 (dd, $J_{Pt,H}$ = 104.63, H-1), 1.46–1.53 (m, H-7), 1.28 (d, $J_{Pt,H}$ = 82.43, $J_{H,H}$ = 10.3, H-1), 1.1 (brs, $J_{Pt,H}$ = 112.96, H-2). ^{195}Pt NMR ($CDCl_3$): 1253 ppm.

Reaction of 3 with H_2. A suspension of dimer **3** (42 mg, 0.06 mmol) in 3 mL of chloroform was placed in a pressure reaction bomb under hydrogen (50 psi). After 24 h, the reaction mixture was removed and the black precipitate filtered. Chloroform was removed by distillation and the resultant yellow oil chromatographed on silica gel with diethyl ether giving 13 mg of **4** in 82% yield: ^1H NMR ($CDCl_3$) 3.5 (ddd, $J_{H,H}$ = 11.0, 1 H), 2.18 (m, 1 H), 1.5–1.82 (m, 6 H), 1.25–1.32 (m, 2 H), 1.06 (d, $J_{H,H}$ = 6.2, 3 H); ^{13}C NMR ($CDCl_3$) 67.78 (d), 41.21 (d), 37.57 (t), 34.85 (t), 26.55

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(16) Vasil'ev, A. A.; Luzikov, Y. N.; Balenkova, E. S. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *20*, 917.

(17) Wittig, G.; Wingler, F. *Chem. Ber.* **1964**, *97*, 2146.

(t), 25.46 (t), 20.29 (q); MS *m/e* (%) 134 (1.2), 132 (2.1), 96 (65.4), 81 (95.9), 55 (100). This is a known compound.[10]

Reaction of 3 with Ph_3P. To 34 mg (0.05 mmol) of **3** in 0.5 mL of $CDCl_3$ was added 24.8 mg of Ph_3P (0.10 mmol) at room temperature to give **5** as a yellow solution. This product was not isolated as it decomposes on purification: ^1H NMR ($CDCl_3$) 6.20 (brs, $J_{Pt,H}$ = 42.01, H-5), 5.67 (brs, $J_{Pt,H}$ = 51.12, H-4), 4.5 (dd, $J_{H,H}$ = 4.3, 3.81, H-3), 2.54–2.61 (m, H-6), 2.8–2.9 (m, H-6), 2.25 (m, H-7), 1.74 (brm, $J_{Pt,H}$ = 95.91, H-2), 1.36 (m, H-7), 1.2 (m, $J_{Pt,H}$ = 105.72, H-1), 0.61 (d, $J_{Pt,H}$ = 62.62, H-1); ^{195}Pt NMR ($CDCl_3$) 680, 601.5 ($J_{Pt,P}$ = 4255); ^{31}P NMR ($CDCl_3$) 21.43 (t, $J_{Pt,P}$ = 4255).

Reaction of 3 with CH_3OH. Methanol (0.5 mL) was added to 50 mg (0.069 mmol) of dimer **3** at room temperature. Stirring was continued until all the dimer was taken up (NMR) to yield **6a** (R = CH_3). Product was not isolated as it decomposed on workup. By ^1H NMR spectroscopy, product **6a** was formed in quantitative yield. ^1H NMR (CD_3OD): 4.32 (brs, $J_{Pt,H}$ = 75.8, H-5), 3.72 (brs, $J_{Pt,H}$ = 88.7, H-4), 3.18 (dd, $J_{H3,H2}$ = 4.2, H-3), 1.95 (m, H-6); 1.85 (m, H-6), 1.5 (m, H-7), 1.35 (dd, $J_{Pt,H}$ = 103.9, H-1), 0.85 (m, H-7), 0.66 (d, $J_{Pt,H}$ = 92.5, $J_{H,H}$ = 10.1, H-1), 0.64 (brs, $J_{Pt,H}$ = 113.5, H-2). ^{13}C NMR (CD_3OD): 81.2 (d, $J_{Pt,C}$ = 50.4, C-3), 78.9 (d, $J_{Pt,C}$ = 255.8, C-5), 76.7 (d, $J_{Pt,C}$ = 273.7, C-4), 56.9 (OCD_3), 50.8 (OCD_3), 32.3 (d, $J_{Pt,C}$ = 31.5, C-2), 22.0 (t, $J_{Pt,C}$ = 40.2, C-6), 20.6 (t, C-7), 7.1 (t, $J_{Pt,C}$ = 646.4, C-1). ^{195}Pt NMR (CD_3OD): 1244.5 ppm.

Reaction of 6a (R = Me) with H_2. To **3** formed from 29 mg (0.31 mmol) of **1** and 90.6 mg of Zeise's dimer were added 2 mL of chloroform and 3 mL of methanol to form **6a**, which was placed in a pressure reaction bomb with 50 psi of hydrogen. After 24 h, the mixture was removed and the black precipitate was filtered off. Solvent was removed by distillation and the resulting yellow oil chromatographed on silica gel with diethyl ether; removal of solvent yielded 32 mg of **7a** (R = Me) in 84% yield: ^1H NMR ($CDCl_3$) 3.3 (s, 3 H), 2.63 (ddd, $J_{H,H}$ = 9.1; coupling of the carbinol proton resonance when methylene protons are irradiated, 1 H), 2.06 (m, 1 H), 0.98–1.74 (m, 8 H), 0.953 (d, $J_{H,H}$ = 6.2, 3 H); ^{13}C NMR ($CDCl_3$) 85.37 (d), 56.23 (q), 38.22 (d), 33.87 (t), 30.48 (t), 25.57 (t), 24.92 (t), 18.68 (q); MS *m/e* (%) 128 (M^+, 29.1), 96 (26), 85 (52), 71 (100). HRMS: calcd for $C_8H_{16}O$, *m/e* 128.1201; found, *m/e* 128.1192.

The same procedure was used when R = Et and isopropyl to give **7b** and **7c** in 82 and 81% yields, respectively.

7b (R = Et): ^1H NMR ($CDCl_3$) 3.62 (dq, 1 H), 3.45 (dq, 1 H), 2.71 (ddd, $J_{H,H}$ = 9.5, 1 H), 2.04 (m, 1 H), 1.05–1.78 (m, 11 H), 0.952 (d, $J_{H,H}$ = 6.2, 3 H); ^{13}C NMR ($CDCl_3$) 83.83 (d), 63.99 (t), 38.41 (d), 34.06 (t), 31.57 (t), 25.67 (t), 25.12 (t), 18.78 (q), 15.69 (q); MS *m/e* (%) 142 (M^+, 57.6), 99 (72.6), 85 (100). HRMS: calcd from $C_9H_{18}O$, *m/e* 142.1358; found, *m/e* 142.1312.

7c (R = *i*-Pr): ^1H NMR ($CDCl_3$) 3.6 (qq, 1 H), 2.73 (ddd, $J_{H,H}$ = 9.1, 1 H), 1.94 (m, 1 H), 1.05–1.73 (m, 14 H), 0.934 (d, $J_{H,H}$ = 6.2, 3 H); ^{13}C NMR ($CDCl_3$) 81.87 (d), 69.76 (d), 38.71 (d), 34.16 (t), 32.92 (t), 25.70 (t), 25.25 (t), 23.68 (q), 22.33 (q), 18.94 (q); MS *m/e* (%) 156 (M^+, 43), 114 (88.9), 57.0 (100). HRMS: calcd for $C_{10}H_{20}O$, *m/e* 156.1514; found, *m/e* 1491.

Reaction of 6a with Ph_3P. To **3**, formed from 35 mg (0.37 mmol) of **1** and 103.9 mg of Zeise's dimer, was added 7 mL of methanol and 2 mL of chloroform with stirring for 10 min to give **6a** as a yellow solution. Triphenylphosphine (92.7 mg, 0.35 mmol) was added and stirred for 28 h. The solution was filtered, removing the yellow precipitate, and solvent was removed by distillation. Chromatography of the resulting oil on silica gel with 10% Et_2O/pentane followed by removal of the solvent gave 35.3 mg of **8a** (80% yield): ^1H NMR ($CDCl_3$) 5.69–5.83 (m, 2 H), 3.36 (d, $J_{H,H}$ = 6.44, residual coupling of the carbinol proton resonance when the vinyl proton is irradiated, 1 H), 3.34 (s, 3 H), 1.95–2.06 (m, 2 H), 1.64–1.76 (m, 1 H), 1.14–1.41 (m, 2 H), 0.984 (d, $J_{H,H}$ = 6.2); ^{13}C NMR ($CDCl_3$) 130.08 (d), 126.68 (d), 81.43 (d), 55.65 (q), 33.11 (d), 28.19 (t), 24.39 (t), 18.24 (q); MS *m/e* (%) 126 (M^+, 19.9), 111 (10.9), 94 (7.8), 84 (100). HRMS; calcd for $C_8H_{14}O$, *m/e* 126.1045; found, *m/e* 126.1033. The same procedure was used for R = Et and isopropyl to give **8b** and **8c** in yields of 79 and 78%, respectively.

8b (R = Et): ^1H NMR ($CDCl_3$) 5.65–5.79 (m, 2 H), 3.38–3.64 (m, 3 H, $J_{H,H}$ = 6.6, for carbinol proton), 1.95–2.06 (m, 2 H), 1.65–1.74 (m, 2 H), 1.14–1.4 (m, 4 H), 0.98 (d, Me); ^{13}C NMR ($CDCl_3$) 129.58 (d), 127.52 (d), 80.09 (d), 63.60 (t), 33.64 (d), 28.42 (t), 24.47 (t), 18.34 (q), 15.69 (q); MS *m/e* (%) 140 (M^+, 19.1), 112 (12.1), 99 (8.3), 98 (100). HRMS: calcd for $C_9H_{16}O$, *m/e* 140.1201; found, *m/e* 140.1184.

8c (R = *i*-Pr): ^1H NMR ($CDCl_3$) 5.58–5.77 (m, 2 H), 3.6–3.72 (m, 1 H), 3.45 (brd, $J_{H,H}$ = 7.1, 1 H), 1.94–2.05 (m, 2 H), 1.6–1.78 (m, 2 H), 1.1–1.4 (m, 7 H), 0.98 (d, 3 H); MS *m/e* (%) 154 (M^+, 3.0), 112 (79.4), 95 (36.7), 79 (22.9), 70 (100). HRMS: calcd for $C_{10}H_{18}O$, *m/e* 154.1358; found, *m/e* 154.1327.

Formation of 7b and 7c via 6a. To 5 mg (0.19 mmol) of **3** was added 1 mL of $CDCl_3$ and 2 mL of MeOH, which formed **6a** as deduced by NMR spectroscopy. After rotoevaporation of the solvent, MeOH, a yellow oil persisted to which was added 3 mL of ROH (R = Et or *i*-Pr) in 2 mL of $CDCl_3$. The solution was stirred at room temperature for 0.5 h and subjected to 50 psi of H_2 for 24 h at room temperature with stirring. Workup was performed as for the production of **7a** to yield **7b** (22 mg, 81% yield) and **7c** (26 mg, 87% yield). These are known compounds.

Formation of 9a. To **3**, formed from 18 μL (16.4 mg, 0.17 mmol) of **1** and 51.3 mg of Zeise's dimer, were added 2 mL of chloroform and 3 mL of methanol at room temperature. After 0.5 h at room temperature the yellow solution containing newly formed **6a** was placed in a pressure reaction bomb and CO (250 psi) was introduced. The mixture was stirred for 2.5 days at 15 °C. After the bomb was vented, the mixture was removed and the black precipitate filtered. The solvent was removed, leaving a yellow oil which was chromatographed on silica gel with diethyl ether. Removal of the ether by distillation yielded 26 mg of **9a** (92% yield): IR ($CDCl_3$) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) (**9a**) 5.79 (brd, 1 H), 5.72 (brd, 1 H), 3.63 (s, 3 H), 3.49 (d, 1 H, $J_{H,H}$ = 6.3, carbinol proton), 3.30 (s, 3 H), 2.50 (dd, $J_{H,H}$ = 5.5, 14.1, 1 H), 2.18 (dd, $J_{H,H}$ = 5.4, 14.1, 1 H), 2.13 (m, 1 H), 2.0 (m, 2 H), 1.80 (m, 1 H), 1.40 (m, 1 H); ^{13}C NMR ($CDCl_3$) 173.4 (s), 130.2 (d), 126.1 (d), 78.9 (d), 55.4 (q), 5.14 (q), 37.3 (t), 35.4 (d), 25.8 (t), 24.2 (t); MS *m/e* (%) 184 (M^+, 2.6), 169 (10.2), 153 (5.7), 152 (7.8), 137 (11.1), 124 (16.1), 110 (74.7), 84 (100). HRMS: calcd for $C_{10}H_{16}O_3$, *m/e* 184.1099; found, *m/e* 184.1045.

Reaction of 3 with Pyridine. Complex **3**, 40 mg, and 1.0 mL of pyridine-d_5 were cooled to 0 °C and then mixed, yielding **10** as a yellow solution in quantitative yield (by NMR). Complex **10** was stable for 1–2 days at room temperature and was not purified further: ^1H NMR (pyridine-d_5) 6.24 (dd, $J_{H,H}$ = 4.7, H-3), 4.00 (dd, $J_{Pt,H}$ = 88.0, H-4), 3.94 (dt, $J_{Pt,H}$ = unres, H-5), 2.70 (ddd, $J_{Pt,H}$ = 93.1, $J_{H,H}$ = 9.5, H-1), 2.55 (m, H-6), 2.30 (m, H-6), 1.86 (brs, $J_{Pt,H}$ = 63.4, $J_{H,H}$ = 4.7, H-2), 1.80 (d, $J_{Pt,H}$ = 90.4, $J_{H,H}$ = 9.5, H-1), 1.35 (m, H-7), 0.9 (m, H-7); ^{195}Pt (pyridine) 1890 ppm; ^{13}C NMR (pyridine) 150.8, 145.1, 143.8, 138.2, 128.1, 125.9 (pyridine resonances) (see Table I for remaining assignments).

Formation of 11a. Cyclopropane **11a** was synthesized by a modification of Tomilov et al.[18] Cyclopentadiene (1.6 g, 24 mmol) was reacted at −10 °C with CH_2N_2 in the presence of a catalytic amount of $(PhCN)_2PdCl_2$ over a period of 1 h. The CH_2N_2 was generated by addition of 5.5 g (25.1 mmol) of diazald in CH_2Cl_2 to 2 g of KOH in 5 mL of water and 12 mL of carbitol as a solvent. Over the course of the reaction three increments of Pd catalyst were added. The mixture was allowed to stir an additional 8 h and chromatographed on silica gel with 5% Et_2O/pentane. Preparative GC (column temperature = 80 °C) was performed to remove cyclopentadiene dimer, giving 0.96 g of **11a** (50% yield): ^1H NMR ($CDCl_3$) 5.9 (m, 1 H), 5.35 (dd, 1 H), 2.56 (dd, 1 H), 2.26 (dd, 1 H), 1.74 (m, 1 H), 1.52 (m, 1 H), 0.75 (ddd, 1 H), −0.2 (dd, 1 H); ^{13}C NMR ($CDCl_3$) 134.8 (d), 127.5 (d), 35.8 (d), 23.5 (t), 16.5 (d), 15.0 (t). HRMS: calcd for C_6H_8, *m/e* 80.0626; found, *m/e* 80.0611.

Formation of 11b. To 10 mg (0.12 mmol) of **11a** in 0.5 mL of $CDCl_3$ was added 36.5 mg (0.06 mmol) of Zeise's dimer at room temperature with stirring for 0.5 h. NMR spectroscopy revealed **11b** in quantitative yield. Addition of pentane caused precipitation of a white solid in 90% isolated yield. Decomposition of **11b** occurs in 5 h: ^1H NMR ($CDCl_3$) 4.46 (brd, $J_{H,H}$ = 3.8, H-3), 4.43 (brs, $J_{Pt,H}$ = unres, H-5), 4.28 (brs, $J_{Pt,H}$ = 87.2, H-4), 1.97 (d, $J_{H,H}$ = 13.6, H-6), 1.69 (dd, $J_{H,H}$ = 13.6, H-6), 1.45 (d, $J_{H,H}$ = 8.1, $J_{Pt,H}$

(18) Zelinski, N. D. Institute of Organic Chemistry Academy of Sciences of the USSR, Moscow, p 533. Translated from: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1984, No. 3, p 582.

= 106.2, H-1), 1.16 (brs, $J_{Pt,H}$ = 80.5, H-2), 0.76 (brd, $J_{H,H}$ = 8, $J_{Pt,H}$ = 113.2, H-1); ^{195}Pt NMR ($CDCl_3$) 1090 ppm. ^{13}C NMR ($CDCl_3$): see Table II.

Formation of 12a. Cuprous chloride (11.5 g, 116 mmol) and 7.6 g (116 mmol) of Zn dust were placed in a two-necked round-bottom flask containing 150 mL of dry diethyl ether. The mixture was charged with nitrogen and refluxed for 0.5 h with stirring. After 30 min 4.7 mL (58 mmol) of 1,3-cycloheptadiene was introduced into the flask followed by 5.2 mL (63 mmol) of diiodomethane. The flask was recharged with nitrogen and refluxed for 26 h. The mixture was cooled to room temperature and filtered into a separatory funnel. A 0.1 N HCl solution was slowly added and the ether washed two times with acid and once with water. The ether layer was dried ($MgSO_4$) and reduced under vacuum. Preparative GC (column temperature = 120 °C) yielded 2.7 g of **12a** as the 2nd fraction (43% yield): ^{1}H NMR ($CDCl_3$) 5.72 (m, 1 H), 5.38 (m, 1 H), 2.0 (m, 2 H), 1.85 (m, 1 H), 1.6 (m, 1 H), 1.45 (m, 2 H), 1.28 (m, 1 H), 1.12 (m, 1 H), 0.75 (ddd, 1 H), 0.1 (dd, 1 H); MS *m/e* (%) 108 (M^+, 33.6), 93 (75.7), 91 (90.9), 80 (55.9), 79 (100). HRMS: calcd for C_8H_{12}, *m/e* 108.0939; found, *m/e* 108.0954.

Formation of 12b. In a 5-dram vial were placed 61.7 mg (0.57 mmol) of **12a**, 4 mL of dry diethyl ether, and 161 mg (0.27 mmol) of Zeise's dimer. The mixture was stirred for 1 h at room temperature at which time a white precipitate had formed. The solid was filtered out and washed two times with 5 mL of pentane and dried under vacuum yielding 39 mg of **12b** (91% yield). Anal. Calcd for $C_{16}H_{24}Cl_4Pt_2$: C, 25.67; H, 3.21; Cl, 18.98. Found: C, 25.60; H, 3.16; Cl, 18.80. ^{1}H NMR ($CDCl_3$): 4.82 (dd, $J_{H,H}$ = 3.81, H-3), 4.73 (brd, 1 H), 4.66 (brd, 1 H), 1.3-2.1 (m, 9 H). ^{13}C NMR ($CDCl_3$): see Table II.

Formation of 13a. Cyclopropane **13a** was formed in a manner analogous to that for **11a** using 1,3-cyclooctadiene (65% yield): ^{1}H NMR[19] ($CDCl_3$) 5.67 (m, 1 H), 5.40 (brd, $J_{H,H}$ = 12, 1 H), 2.42 (m, 1 H), 1.95 (m, 3 H), 1.6 (m, 2 H), 1.2-1.45 (m, 2 H), 0.75-1.0 (m, 2 H), 0.7 (ddd, 1 H), -0.2 (dd, 1 H); ^{13}C NMR ($CDCl_3$) 134.5 (d), 126.7 (d), 31.3 (t), 29.6 (t), 28.0 (t), 25.8 (t), 19.2 (d), 14.6 (d), 10.5 (t). HRMS: calcd for C_9H_{14}, *m/e* 122.1095; found, 122.1115.

Formation of 13b. Zeise's dimer (124.7 mg, 0.21 mmol) was added to a 25-mL round-bottom flask containing 56.9 mg (0.46 mmol) of **13a** and solvent. The following conditions were tried: (A) Diethyl ether at room temperature for 8 h; (B) refluxing diethyl ether for 8 h; (C) refluxing chloroform under nitrogen for 18 h; (D) refluxing toluene for 2 h under nitrogen; (E) 250 mg of Zeise's dimer in refluxing diethyl ether for 10 h. The above experiments were all run with 10-15 mL of solvent with continuous stirring. At the end of the reaction pentane was added, precipitating an orange solid. The solid was generally washed a total of three times with pentane and then dried under vacuum. The precipitate was characterized by NMR in $CDCl_3$, which gave broad resonances due to the platinum. Addition of pyridine sharpened the signal and enabled platinum coupling to be measured. The pyridine solutions were unstable and decomposed to Py_2PtCl_2 and **13a** over a period of 8 h. Data for **13b**: ^{1}H NMR ($CDCl_3$) 5.8 (m, 1 H, $J_{Pt,C}$ = 70), 5.3 (dd, 1 H, $J_{Pt,C}$ = 69), 2.4-2.7 (m, 6 H), 1.55-1.85 (m, 3 H), 1.0 (m, 1 H), 0.7 (dd, 1 H), 0.2 (dd, 1 H); ^{13}C NMR ($CDCl_3$) 96.9 (d, $J_{Pt,C}$ = 152.6), 90.6 (d, $J_{Pt,C}$ = 156.0), 31.1 (t), 30.9 (t), 28.6 (t, 2 C), 22.9 (d), 14.9 (d), 13.6 (t).

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Notes

Identification of a Surface Organometallic Species Anchored on a Thiourea-Functionalized Silica Xerogel. Crystal Structure of the Model Compound $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$

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Summary: $Ru_3(CO)_{12}$ reacts with a thiourea-functionalized silica xerogel, derived from $(EtO)_3Si(CH_2)_3NHC(=S)NHPh$, to give a tethered metal carbonyl cluster. This surface organometallic species has the same CO stretching pattern as that of the model compound $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$ (**1**), obtained from the reaction of $Ru_3(CO)_{12}$ with *N*-phenyl-*N'*-propylthiourea. The molecular structure of **1** has been fully elucidated by an X-ray diffraction study.

Transition-metal carbonyl clusters can be used both as heterogeneous catalyst precursors and as homogeneous catalysts themselves, for a variety of reactions.[1] Their immobilization by tethering to organic or inorganic solids yields systems that combine the advantages of both homogeneous and heterogeneous catalysts.[2] The active sites are discrete complexes, whose mechanism of action is similar to that of their truly homogeneous counterparts, but at the same time the ease of separation and recovery which characterize heterogeneous catalysts are retained. These systems have been prepared by a variety of routes, mostly inferred from organometallic solution chemistry of the suitable functional group present on the surface.[3] The phosphine group[4] anchored to silica is the most common

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