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Reaction of Ziese's Dimer with *endo*-Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene and Subsequent Rearrangements

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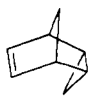
Zeise's dimer reacts rapidly with *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene to form the nortricycloplatinacyclopentane complex **3**. Further, treatment of **3** with Ph_3P effects a carbocyclic rearrangement that is analogous to a cyclopropylcarbinyl system.

Introduction

Recently we reported[1,2] that *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene reacted with Zeise's dimer $(C_2H_4PtCl_2)_2$ to form the first isolated example of a cis-2,3-disubstituted platinacyclobutane complex. We now wish to report on the endo isomer **1** which reacts to form a nortricyclometallacyclopentane presumably via an unstable metallacyclobutane intermediate. Subsequent reaction of the metallacyclopentane complex with Ph_3P induces a carbocyclic rearrangement that appears to be analogous to a cyclopropylcarbinyl cationic rearrangement.

Results and Discussion

As expected, the endo isomer **1** reacted with a suspension of Zeise's dimer in ether to form the typical yellow precipitate **2**. This complex was initially assumed to be a platinacyclobutane complex. Complex **2** reacted further with pyridine in $CHCl_3$ to form the soluble complex **3**. The first indication that this reaction had not proceeded in a similar fashion as the exo isomer occurred when we obtained the solution and solid-state ^{13}C NMR spectra of these two complexes (Figure 1). Examination of these spectra revealed the significant fact that neither one exhibited an olefinic resonance. The resonances at 125, 138, and 151 ppm in spectrum B are due to the two nonequivalent pyridine ligands. Had the reaction behaved as usual, structure A or B would have been formed and olefinic absorptions would have been apparent in the 60–140 ppm range.[1,2] Thus, if one ignores the pyridine and chloroform resonances in spectrum B, it consists of eight lines in the saturated carbon region with two of them showing coupling to ^{195}Pt as indicated by x and y. The ^1H and ^{13}C NMR data for complex **3** are listed in Table I.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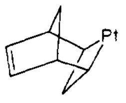

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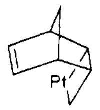

B

The structure shown in Figure 1 is proposed for **3** and appears to be consistent with the spectral data as discussed herein. For example, the lack of symmetry in **3** is consistent with an eight-line spectrum. The cyclopropane carbons (5–7) are also evident by their coupling constants to protons (typically 170 Hz). The chemical shift positions for these carbons are downfield of what one might expect. However, in these systems, the range of ^{13}C chemical shifts for methine carbons range from 23.1 to 9.4 ppm.[1,2,10] Further, from the gated decoupled ^{13}C spectrum, there are only two methylene resonances (1 and 8) with only one of them being coupled to ^{195}Pt. These data along with the lack of an olefinic moiety, proton–proton decoupling experiments, selective proton–carbon decoupling data, and comparison to known compounds[1,2,10] lead us to conclude that the structure for **3** is indeed the metallacyclopentane complex shown in Figure 1.

The spectrum shown in Figure 1 as A is the MAS/CP ^{13}C NMR spectrum of the initial precipitate **2**. As we have previously observed, on comparing B to A, one finds that all of the resonance lines of B are accounted for in the broad unresolved resonances of A except for the two low intensity resonances at 39.7 and 66.8 ppm. These reso-

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(1) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 385–387.

(2) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370.

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Table I. ^{13}C and ^{1}H NMR Spectral Data for Complex 3

	^{13}C data[a]			^{1}H data			
atom	chem shift, ppm	J_{Pt-C}, Hz	J_{C-H}, Hz	chem shift, ppm	J_{Pt-H}, Hz	mult	J_{H-H}, Hz
1	21.5 (t)	535	138	3.75[b]	85	dd	7.3, 3.8
				3.01[b]	82	d	7.3
2	48.3 (d)	···	129	0.60[b]	38	br s	3.8, 1.3, 1.3
3	46.2 (d)	14	147	2.80[b]		br s	1.3
4	44.2 (d)	574	144	2.14[b]	82	mult	1.3, 1.3, 1.3
5	21.0 (d)	24	178	1.92[b]		br t	ddd 5.1, 5.1, 1.3
6[c]	19.6 (d)	22	169	1.24		br t	ddd 5.1, 5.1, 1.3
7	17.6 (d)	37	173	1.34		obscured	
8a	29.8 (t)	37	131	1.41		d	10.7
8b				1.33		d	10.7

[a] Pyridine ligands are not equivalent and resonate at 150.7 and 150.9, 125.5 and 125.2, and 138.3 and 138.0. [b] Proton selectively decoupled with ^{13}C observed. [c] Resonances for C(6) and C(7) may be interchanged.

Table II. ^{13}C and ^{1}H NMR Data for Complex 4

	^{13}C data			^{1}H data		
atom	chem shift, ppm	J_{Pt-C}, Hz	J_{C-H}, Hz	chem shift, ppm	J_{Pt-H}, Hz	mult
1	72.9 (d)	271	171	3.32[a]	54	br s
2	67.9 (d)	276	171	3.23[a]	54	br s
3	56.2 (d)	<10	148	2.05		obscured
4	58.5 (d)	75	156	3.91[a]		br d
5	38.9 (t)	43	137	1.8-2.05	(exo, endo)	obscured
6	46.5 (d)	<10	148	1.76[a]		br s
7	49.7 (d)	<10	136	0.70[a]	100	br s
8	23.1 (t)	575	138	0.92	63	AB

[a] This reaction mixture has excess Ph_3P that leads to broadening of these resonances.

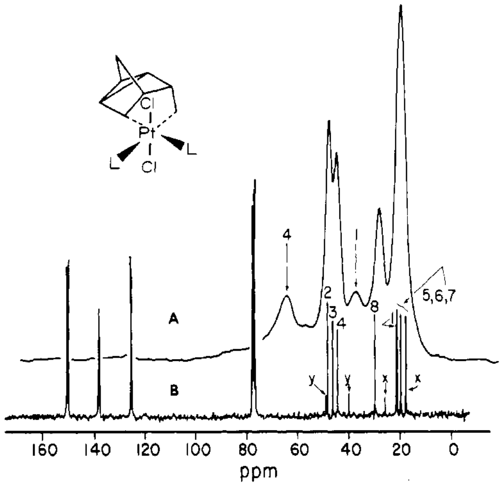
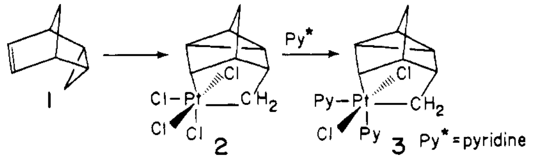


Figure 1. ^{13}C NMR spectra for complexes 2 and 3. A is the magic angle spinning/cross polarization spectrum, and B is the solution spectrum of the pyridine-solubilized complex.

nances are assigned to carbon atoms 1 and 4 and correspond to the solution resonances at 21 and 44.2 ppm, respectively. This apparent chemical shift difference is due to a change in ligands from pyridine to Cl and has been discussed previously.[2] It is therefore concluded that the organic moiety in structures 2 and 3 are identical. Thus, the proposed reaction of 1 is shown as eq 1.



(1)

Rearrangement of 3. Treatment of compound 3 with Ph_3P should have produced the original hydrocarbon. However, a new complex, 4, was obtained which contained platinum as evidenced by its substantial coupling to three carbon atoms 1, 2, and 8 (Table II). Furthermore carbons 1 and 2 have chemical shifts of 73 and 68 ppm, which is reasonable for a metal complexed olefin.[2] Crystals of this complex, which were readily obtained, were subsequently submitted for X-ray crystallographic analysis. Two perspective views of this compound are shown in Figure 2 with selected bond lengths and angles and atomic coordinates listed in Tables III and IV.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

Bond Lengths			
Pt-C(1)	2.154 (15)	C(1)-C(2)	1.428 (25)
Pt-C(2)	2.119 (16)	C(5)-Cl(2)	1.807 (14)
Pt-C(8)	2.077 (15)	Pt-P(1)	2.424 (5)
Pt-Cl(1)	2.451 (4)	Pt-P(2)	2.385 (4)
Bond Angles			
C(1)-Pt-C(2)	39.0 (7)	P(1)-Pt-P(2)	107.3 (2)
Cl(1)-Pt-C(8)	167.7 (4)	Pt-C(8)-C(7)	108.0 (11)

Table IV. Selected Atom Coordinates for the Non-Hydrogen Atoms

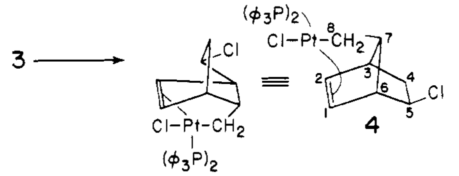
atom	*x*	*y*	*z*
Pt	10371 (6)	26254 (5)	9725 (6)
Cl(1)	1917 (3)	4557 (3)	382 (3)
Cl(2)	−3675 (4)	893 (5)	4435 (5)
P(1)	2312 (3)	1860 (3)	1940 (4)
P(2)	1949 (3)	2829 (3)	1031 (3)
C(1)	−469 (13)	2788 (12)	2308 (13)
C(2)	−543 (12)	3219 (12)	1178 (13)
C(3)	−1477 (12)	2416 (12)	1305 (15)
C(4)	−2631 (15)	2550 (16)	2177 (16)
C(5)	−2503 (13)	2062 (15)	3356 (16)
C(6)	−1327 (12)	1681 (12)	3073 (12)
C(7)	−1267 (11)	1260 (12)	2136 (12)
C(8)	−24 (12)	1142 (11)	1491 (13)

There are three minor areas of interest in this structure. First of all, the Pt–C(1) bond distance appears to be slightly longer than Pt–C(2) even though the standard deviations tend to minimize this difference. This could, of course, be due to crystal packing forces. However, even in solution there are differences between C(1) and C(2) as evidenced by their ^{13}C chemical shift positions at 72.9 and 67.9 ppm, respectively. Moreover, the J_{Pt-C} coupling constant to C(1) is less than that to C(2) which would be consistent with a bond length difference. The most obvious perturbation on that side of the system is the transannular chlorine atom that is most certainly withdrawing electron density at C(1) giving the results observed.

A second point of interest is that the Cl(1)–Pt–C(8) bond angle which is 167° rather than 180°. This deviation is most likely due to the forces exerted by the bulky triphenylphosphine groups.

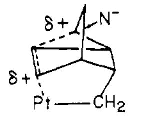
Finally, we would like to call the reader's attention to the Pt–C coupling constants to the olefinic carbons. These values (270 Hz) are certainly too large to accommodate a simple π complex that has values on the order of 100–150 Hz. On the other hand they fall short of Pt–C σ bonds that typically range from 350 to 650 Hz.[1-3] While we would like to suggest that complex **4** is a metallacyclopropane, the evidence is not overwhelming. Thus, the best attitude to take at this time is that there is considerable backbonding in this complex. In a subsequent section of this paper, attention will again be drawn to this idea when complex **5**, which has one less phosphine ligand, is discussed.

Rearrangement of 3 to 4. This carbocyclic rearrangement, **3** to **4**, appears to be related to the cyclopropyl cationic rearrangements which are associated with this bicyclic series (eq 2). In the hydrocarbon system, the



(2)

intermediate cation shown as structure **7** is conjugated to



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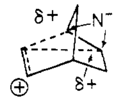

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the cyclopropyl moiety[4,5] resulting in equal attack at either carbon by a nucleophile. Presumably in this case, the leaving group is far from the original cationic site allowing for equal conjugation by both sides of the cyclopropane. In the example **3** to **4**, we suggest that the leaving group Pt does not completely leave the original site as it will eventually coordinate to the double bond. Thus, in the organometallic system a free carbocation at C(4) is not produced. Instead, a partially cationic orbital forms with its lobe exo to the main bicyclic system and thereby draws preferential stabilization from the C(5)–C(7) bond of the cyclopropyl moiety. This situation then results in charge density at the bridgehead carbon.

In an effort to provide some data on the ionic character of the rearrangement, the reaction was conducted in the more polar solvent system composed of a 1:1 ratio of $CDCl_3$ to MeOH. From this reaction, which proceeds qualitatively faster, one observes capture of both Cl and MeO at the same position in a ratio of 15:85, respectively. The ^{13}C and ^{1}H data for the methoxy derivative are listed in Table V. Thus with the methoxide capture, it appears reasonable to suggest that there is ionic character to this rearrangement.

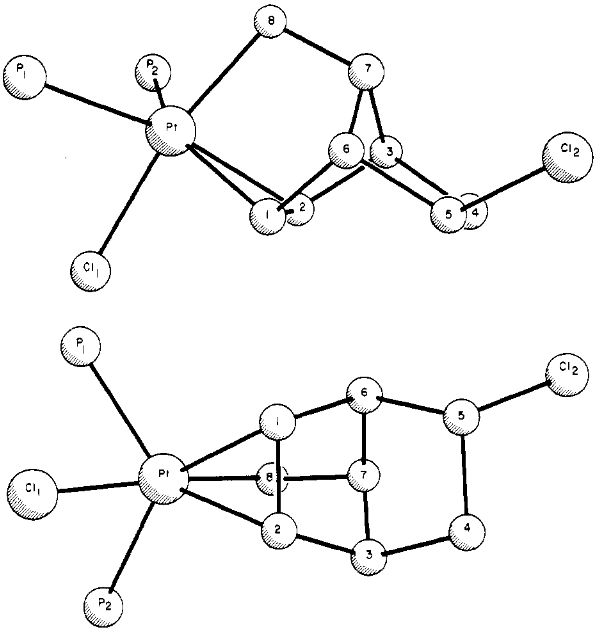
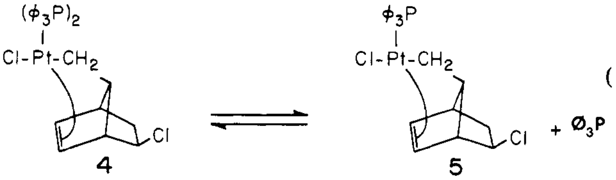


Figure 2. Perspective views of rearrangement product **4**.

Table V. ^{13}C NMR Data for the Methyl Ether Analogue of 4

C no.	δ	J_{Pt-C}, Hz	J_{C-H}, Hz
1	84.5		
2	90.6		
3	47.1 (d)	<10	148
4	33.7 (t)	43	131
5	82.2 (d)	65	148
6	52.8 (d)	<10	149
7	51.1 (d)	···	135
8	24.3 (d)	599	136
9	56.99 (OCH_3)	···	141

Equilibrium between 4 and 5. If to suspension of **2**, 1.4 equiv of Ph_3P are added, the suspension dissolves forming the complex **4** and another complex **5**. It was clear from the ^{1}H and ^{31}P NMR spectra which exhibited broad resonances that some sort of exchange broadening was occurring. On cooling the mixture to −60 °C, sharp resonances for both compounds could be resolved (Table VI). Moreover, the addition of more Ph_3P gave complex **4**. The phosphorus spectrum of **5** consisted of a single resonance at 24.2 ppm which was coupled to ^{195}Pt by 4200 Hz. Likewise, the ^{195}Pt spectrum of **5** was a doublet with J = 4200 Hz. Thus, we suggest that the difference between **4** and **5** is one Ph_3P group and that they are in equilibrium as shown in eq 3. The equilibrium constant ($4 \rightleftharpoons 5$) as measured at 25 °C is 1×10^{-3} M.



(3)

There are a couple of comparisons to note between the ^{13}C spectra of **4** and **5** (Tables II and VI). First of all the

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(4) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 2089.

(5) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Surya Prakash, G. K. *J. Am. Chem. Soc.* **1981**, *103*, 1122.

Table VI. ^1H and ^{13}C NMR Data for Complex 5

	^1H data			^{13}C data[b]		
C=H no.	δ	J_{Pt-H}, Hz	mult	δ	J_{Pt-C}, Hz	$^1J_{C-H}$, Hz
1	5.37	60	br s	108.9	174	. . .
2	5.61	60	br s	116.4	166	. . .
3	2.92		br s	50.4	18	150
4-exo	2.10[a]		ddd	36.7	44	136
4-endo	1.93[a]		dd			
5	3.77		dd	55.9	63	161
6	3.03		br s	59.6	22	148
7	1.55	102	br s	53.7	. . .	139
8	0.84	63	br s	22.6	628	136

[a] $J_{5,4n} = 7.3$ Hz, $J_{5,4x} = 2.6$ Hz, $J_{5,4n} = 7.3$ Hz, $J_{5,4x} = 2.6$ Hz, $J_{4x,4n} = 13.7$ Hz, $J_{4x,3} = 3.8$ Hz, $J_{4x,3n} = 13.7$ Hz, and $J_{4x,3} = 3.8$ Hz. [b] Ph_3P: δ 130 (i), 134.9 (o), 128.7 (m), and 131.2 (p). ^{31}P shows a singlet at 24.2 ppm ($J_{Pt-P} = 4200$ Hz). ^{195}Pt shows a doublet at $J = 4200$ Hz.

olefinic carbon resonances of 5 have shifted downfield by 40 ppm compared to those in complex 4, indicating a reduction in metal complexation.[2] This is further corroborated by the reduction in coupling constant to ^{195}Pt for these atoms. As in complex 4, the olefinic carbons of 5 are not equivalent in solution which again suggests that the chlorine at carbon C(5) is exhibiting a transannular perturbation. We suggest then that complex 5 is a four-coordinate Pt(II) complex.

Summary. In contrast to *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene which yields a stable platinacyclobutane complex that regenerates starting material on treatment with Ph_3P, the endo isomer 1 reacts with Zeise's dimer to yield the insoluble nortricyclometallacyclopentane complex 2. Presumably, a platinacyclobutane complex forms first followed by a facile pseudo 1,3 sigmatropic shift. Reaction of 2 with pyridine gives the solubilized nortricyclometallacyclopentane complex 3. Subsequent treatment of 3 with 2–3 equiv of Ph_3P gave the rearrangement product 4 whiich has been characterized by X-ray crystallography and NMR spectroscopy. Finally, in solution with a deficient supply of Ph_3P, complex 4 was shown to be in equilibrium with the monophosphine complex 5.

Experimental Section

General Data. Solution NMR spectra were obtained in $CDCl_3$ by using a Bruker WM 250 spectrometer. The solid-state NMR spectrum was acquired at the NSF regional facility at Colorado State University. K_2PtCl_4 and Ph_3P were obtained from Aldrich and used without further purification. $CDCl_3$ was obtained from Stohler and used as supplied. Elemental analyses were performed by Galbraith Laboratories. Zeise's dimer was prepared from K_2PtCl_4 by the method of Littlecott.[6] Yields via silica chromatography were not optimized.

Preparation of 1. Compound 1 was prepared by the method of Closs[7] and purified by preparative GC using a 10 ft × 0.25 in. column packed with 5% SE30. Spectral data agreed with the literature.

Preparation of 2. To a flask containing 295 mg (0.5 mmol) of $(C_2H_4PtCl_2)_2$ suspended in 10 mL of dry Et_3O was added 170 mg (1.6 mmol) of 1. As the orange dimer was consumed, the typical yellow precipitate formed during the 10-min stirring period. From the precipitate which was filtered, washed with EtOH, and dried by suction and vacuum dessication, 356 mg (96% yield) of the yellow complex 2 was obtained; mp 147 °C. Anal. Calcd for $C_8H_{10}PtCl_2$: C, 25.82; H, 2.71. Found: C, 25.63; H, 2.84.

Preparation of 3. To a suspension of 2 in 10–15 mL of $CHCl_3$ was added 2.5–3.0 equiv of pyridine dropwise with stirring. After ca. 15 min, the yellow solution was rotoevaporated at 30 °C to yield a dark yellow oil. Addition of pentane and further rotoevaporation afforded a light yellow solid. Trituration in more pentane and rotoevaporation followed by vacuum dessication gave the light yellow complex 3 in nearly quantitative yield; mp 122 °C. Anal. Calcd for $C_{18}H_{20}N_2PtCl_2$: C, 40.76; H, 3.80. Found: C, 40.78; H, 3.87.

Rearrangement of 3 to 4. To 100 mg (0.27 mmol) of 3 in 3 mL of $CDCl_3$ was added 248 mg (0.81 mmol) of Ph_3P. After being stirred 10 min, the resulting light yellow solution was used for ^1H and ^{13}C NMR determinations. The initial proton NMR spectrum was quite complex and indicated a mixture. The ^{13}C NMR was not illuminating for detecting intermediates as the rearrangement to 4 occurred too swiftly at the concentrations required for ^{13}C analysis. As the color of the solution lightened over a period of minutes to several hours, the proton and ^{13}C spectra showed the presence of 4. After 24 h, the proton NMR spectrum showed only 4. Subsequent chromatography on silica with chloroform gave a yellow oil that solidified upon repeated trituration in pentane and rotoevaporation. After drying extensively under vacuum, a 70% yield of the white solid 4 was obtained; mp 225–235 °C. Anal. Calcd for $C_{44}H_{40}P_2PtCl_2$: C, 58.93; H, 4.50. Found: C, 58.98; H, 4.60. The proton-decoupled ^{31}P NMR spectrum of purified 4, at −60 °C, showed two platinum-coupled resonances in an A–B pattern ($^2J_{P,P} = 77$ Hz) at δ 2.21 ($J_{Pt,P} = 2470$ Hz) and at δ 0.21 ($J_{Pt,P} = 2310$ Hz) relative to external H_3PO_4 at 0 ppm at 25 °C. Crystals for X-ray analysis were grown by layering heptane on a $CHCl_3$ solution of 4. Upon standing, crystals of 4 formed at the interface.

Preparation of 5. To a suspension of 298 mg (0.8 mmol) of 2 in 10 mL of $CDCl_3$ was added 293 mg (1.12 mmol) of Ph_3P (corresponding to 1.4 equiv relative to 2). After being stirred for 15 min, the solution was analyzed by NMR spectroscoy and then chromatographed on silica gel by using $CHCl_3$ as solvent. Rotoevaporation of the first major fraction gave a yellow oil that solidified upon repeated trituration in pentane. Following extensive drying in a vacuum dessicator, 208 mg (41% yield) of the white solid 5 was obtained; mp 165 °C. Anal. Calcd for $C_{26}H_{25}PPtCl_2$: C, 49.22; H, 3.97. Found: C, 49.46; H, 4.19. The presence of 4 as the major constituent of a later-eluting chromatographic fraction was determined by NMR spectroscopy and thin-layer chromatography but was not quantitated. Vapor-phase osmometry confirmed complex 5 exists as a monomer. The proton-decoupled ^{31}P NMR spectrum of 5 at room temperature showed a single platinum coupled resonance at 24.2 ppm ($J_{Pt,P} = 4200$ Hz).

Determination of the Equilibrium $4 \rightleftharpoons 5$. The room-temperature ^{31}P NMR spectrum of the previously described reaction mixture from 2 with 1.4 equiv of Ph_3P showed only a broad and nearly undetectable resonance buried under minor impurity peaks. Upon cooling to −60 °C, sharp resonances of 4 and 5 were resolved as the only significant components. The proton NMR spectrum of a mixture of 5 mg of purified 4 and 5 mg of 5 at room temperature showed resonances for only ten nonaromatic protons appearing at intermediate chemical shifts relative to the spectra of 4 and 5 recorded separately. Upon cooling to −40 C, distinct resonances for the CHCl protons of 4 and 5 and somewhat broadened resonances for the vinyl resonances of the two compounds were observed. Saturation of the vinyl proton of one compound resulted in the decrease in integral for a vinyl proton in the second compound, indicating saturation transfer. From these data, the room-temperature equilibrium constant for $4 \rightleftharpoons$

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5 + Ph_3P was determined to be 1×10^{-3} M.

Preparation of the Methoxy Analogue of 4. To a solution of 167 mg (0.3 mmol) of 3 in 100 mL of $CHCl_3$ was added 100 mL of methanol with magnetic stirring. Upon the subsequent addition of 384 mg (1.47 mmol) of Ph_3P, the solution immediately became darker and then lightened in color over a 1–2-h period. Ten hours after the addition of Ph_3P, the solution was rotoevaporated to a yellow oil that when triturated with pentane, rotovapped, and dried under vacuum gave a yellow-white solid. The solid was extracted with 20 mL of Et_2O to remove unreacted Ph_3P and residual methanol. After rotoevaporation and drying under vacuum, 256 mg of a white solid was obtained. A portion of this was dissolved in $CDCl_3$, and sufficient Ph_3P was added to cause an upfield shift in the vinyl proton resonances which avoided obscuring the CHCl proton resonance of 4. Integration of the CHCl resonance of 4 vs. the methoxy analogue resonance gave a 85:15 molar ratio of methoxy analogue to 4. Following the combination of this NMR tube contents with the remainder of the white solid, the material was chromatographed on silica with $CHCl_3$. An early eluting fraction was determined by NMR spectroscopy to contain a mixture of 4 and methoxy analogue, while the major and later eluting fraction, following rotoevaporation, pentane trituration, and drying under vacuum, yielded 118 mg (46%) of the white methoxy analogue; mp 205 °C. Anal. Calcd for $C_{45}H_{43}OP_2Pt$: C, 60.59; H, 4.86. Found: C, 60.37; H, 4.92. Control experiments were run deleting either Ph_3P or MeOH resulting in no significant reaction according to NMR spectroscopy. In addition, solutions of 4 or 5 that were incubated in $MeOH(CHCl_3)$ showed no production of the methoxy analogues.

X-ray Structural Determination of 4. Crystals of 4 were grown at the interface of a heptane/chloroform bilayer and a specimen suitable for X-ray analysis was mounted on a fiber. X-ray data collection was carried out on a Nicolet R3m automated diffractometer equipped with a Mo target X-ray tube ($\lambda = 0.71073$ Å) and a graphite crystal monochromator.[8] Unit cell constants were determined to be $a = 12.804$ (5) Å, $b = 13.061$ (5) Å, $c = 13.416$ (5) Å, $\alpha = 65.95$ (3)°, $\beta = 67.59$ (3)°, and $\gamma = 8.45$ (3)° for a cell of triclinic symmetry. The space group was determined to be $P\bar{1}$. Intensity measurements of 3669 independent reflections for $3 \leq 2\theta \leq 45°$ were observed with $I \geq 3\ \sigma(I)$. Absorption corrections were made by using the empirical psi scan method, and no decay corrections were necessary.

The structure was solved by direct methods that revealed the locations of all non-hydrogen atoms on the initial *E* map. The structure was refined to a final *R* value of 0.065 by a blocked-cascade technique with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters. All structural determinations and refinement calculations were carried out with the SHELXTL package on the Nicolet R3m crystallographic system.[9] A cell mass of 1793.5 containing 892 electrons and two molecules per unit cell gave a calculated density of 1.60 g/cm^3 for $C_{44}H_{40}PtCl_2P_2$. The final difference map revealed no abnormal features.

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Registry No. 1, 3635-94-7; 2, 86834-41-5; 3, 86823-57-6; 4, 86823-58-7; 4 (MeO-deriv.), 86823-60-1; 5, 86823-59-8; $(C_2H_4PtCl_2)_2$, 12073-36-8; Ph_3P, 603-35-0.

Supplementary Material Available: Tables of bond lengths, bond angles, atom coordinates and temperature factors, anisotropic temperature factors, and hydrogen coordinates and temperature factors (5 pages). Ordering information is given on any current masthead page.

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(8) Programs used for centering of reflections, autoindexing, refinement of cell parameters, axial photographs, and data collection were those described in: "Nicolet P3/R3 Data Collection Manual"; Calabrese, J. C., Ed.; Nicolet XRD Corp.: Fremont, CA, 1980.

(9) Programs used for data reduction, Fourier syntheses, direct method structure solution, least-squares refinement, error analysis, least-squares planes calculation, and calculation of hydrogen position are those described in: "Nicolet SHELXTL Structure Determination Manual"; Sheldreck, G. M., Ed.; Nicolet XRD Corp.: Fremont, CA, 1980.

(10) Cheng, A. K.; Stothers, J. B. *Org. Magn. Reson.* **1977**, *9*, 355.

Electronic and Geometric Features of (η^5-C_5H_5)ML 16-Electron Fragments. A Molecular Orbital Study of Ligand Effects

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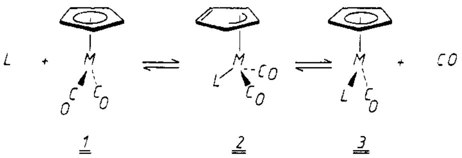
Qualitative MO theory, based upon extended Hückel calculations, is utilized to study coordinatively unsaturated 16-electron fragments d^8 (η^5-C_5H_5)ML (M = transition metal, L = ligand) with respect to their geometric and electronic structure as a function of the ligands L. It is shown that such fragments, observed as reactive intermediates in organometallic reactions, can possess singlet ground states, which then will exhibit "nonlinear" Cp–M–L arrangements. The comparative ease of a number of important reactions proceeding via such intermediates without any spin-imposed high activation barriers can thus be readily understood.

Introduction

Since the early and important kinetic experiments by Basolo and Schuster-Woldan,[1] it has been well-known that d^8 18-electron half-sandwich compounds of the type (η^5-C_5H_5)M(CO)$_2$ (1, M = Co, Rh, Ir) undergo thermal ligand substitution reactions by associative (S_N2) pathways.[2] This puts them in contrast to metal carbonyl complexes

Scheme I



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