Table II. Product Distributions from the Hydrogenolysis of **5**

Catalyst	H_2 flow rate, cm^3 min^{-1}	T, °C	Recovd 5	trans-4 + 2	3	cis-exo-4	cis-endo-4	exo-6	endo-6	Unidentified compds, incl. dimers[a]
2% Pd/pumice	9.5	140	85			2.4	12.2	0.4		
	9.5	195		7.1	0.6	7.5	4.6	56.0	16.2	8.0
	9.5	250		6.5		8.2	10.7	50.4	16.2	9.0
2% Pt/SiO₂	9	82		43.4	23.7	13.5	8.1	5.3	5.3	
	9	140		7.7	1.5	11.5	15.2	38.7	13.7	
	9	242		1.3	0.8	15.6	10.4	38.0	7.5	26.0
PtO₂ in acetic acid	2-mol uptake	30		15.0	85.0					
	1 mol	30	>98% of **1**							

[a] Identified using an MS30 gas chromatographic–mass spectral system.

1

2 + 3 + 4

5

2 + 3 + 4 +

6
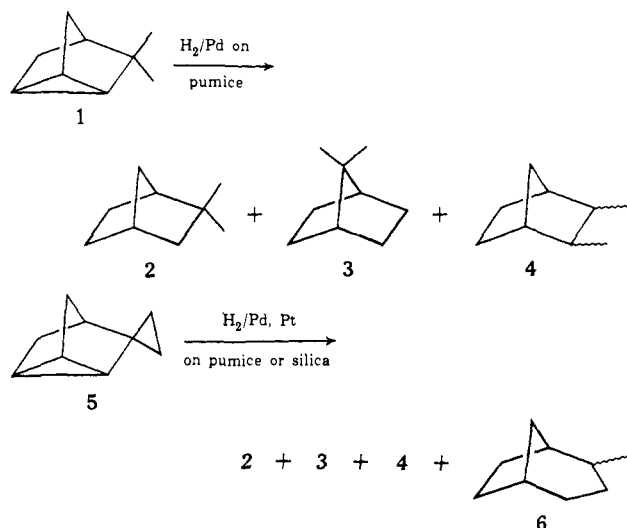
Again, the pumice support was shown to be inactive (at 200°) in the absence of metal. Reactions at higher temperatures, especially over platinum, gave increasing amounts of dimeric (mol wt 244) and oligomeric material.

These are the first examples of 1,2-alkyl shifts during hydrogenolysis of strained C₃-ring hydrocarbons in excess hydrogen over supported metals. The products can be explained by metal insertion into the C₃ ring to give initially a metallocarbonium ion, e.g., **7**. The more

$$1 + M \longrightarrow$$

7
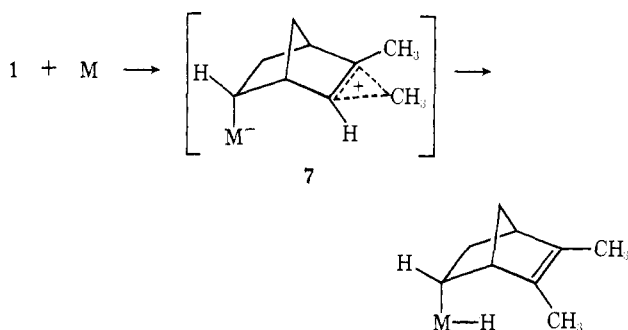
sterically hindered C–C bond of the C₃ ring is preferred because the resulting carbonium ion is stabilized by charge delocalization arising from the simultaneously migrating methyl group. Hydrogenation of 2,3-dimethylbicyclo[2.2.1]hept-2-ene gives mainly the di-endo-methyl compound **4**.[3] The postulated mechanism is very similar to that suggested for isomerizations of strained C₃-ring hydrocarbons homogeneously

(3) K. Alder and W. Roth, Chem. Ber., **88**, 407 (1955).

catalyzed by Ag⁺, Rh⁺, and other metal cations.[4] We are currently investigating why these reactions are so sensitive to catalyst, support, and reaction medium.

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Intermolecular Ligand Exchange in Cationic Nickel, Palladium, and Platinum Hydrides of the Type HML₃⁺X⁻ in the Presence of Added Phosphine Ligand

Sir:

We present, for the first time, direct nmr spectroscopic evidence for the rates of ligand association in a series of four-coordinate group VIII complexes (HML₃⁺ species) relative to the rate of intramolecular rearrangement within the five-coordinate intermediate or transition state (HML₄⁺) (M = Ni(II), Pd(II), Pt(II); L = P(C₂H₅)₃).

The hydride region ¹H nmr spectrum (all nmr parameters are given in Table I) for an acetone-d₆ solution of HPt[P(C₂H₅)₃]₃⁺B(C₆H₅)₄⁻ consists of a doublet of triplets (with ¹⁹⁵Pt satellite lines) indicating that the cation has a square planar structure (1) in solution.[1,2] As P(C₂H₅)₃ is added, the triplets broaden and then sharpen into singlets. The limiting spectrum in the presence of a large excess of ligand is a doublet in which the J_{HP_1} couplings have been lost while the J_{HP_2} coupling has been retained.

The ³¹P{¹H} Fourier mode nmr spectrum (Figure 1) in the absence of added ligand is an A₂B pattern together with an A₂BX pattern (34% ¹⁹⁵Pt). As ligand is added (Figure 1) the resonances assigned to the A spins (L₁) broaden and eventually coalesce with the free ligand resonance. By contrast the resonances assigned to the B spin (L₂) are simply decoupled from the A spins and only slightly broadened by the exchange process. The ¹H and ³¹P data indicate that the Pt–L₁ bond is broken in the exchange process and that there is no concomitant

(1) M. J. Church and M. J. Mays, J. Chem. Soc. A, 3074 (1968).
(2) H. C. Clark and K. R. Dixon, J. Amer. Chem. Soc., **91**, 596 (1969).

Table I. Nmr Spectral Parameters of HM[P(C$_2$H$_5$)$_3$]$_3$$^+$B(C$_6H_5$)$_4$$^-$ Species[a]

| | ———————¹H hydride spectrum——————— | | | | ———————³¹P{¹H} spectrum——————— | | | |
	J_{HP_1}	J_{HP_2}	δH	T, °C	J_{AB}	δ_A	δ_B	T, °C
Ni	±69	∓102	12.39	−73	25	−16.8	−15.1	−90
Pd	~0	182	7.80	−50	31	−20.6	−10.6	28
Pt	15	157	6.04	−50	20	−16.6	−13.4	0

[a] All samples were dissolved in acetone-d_6. Coupling values are given in Hz. Chemical shifts are given in ppm: ¹H is referred to TMS, ³¹P is referred to 85% H$_3$PO$_4$.
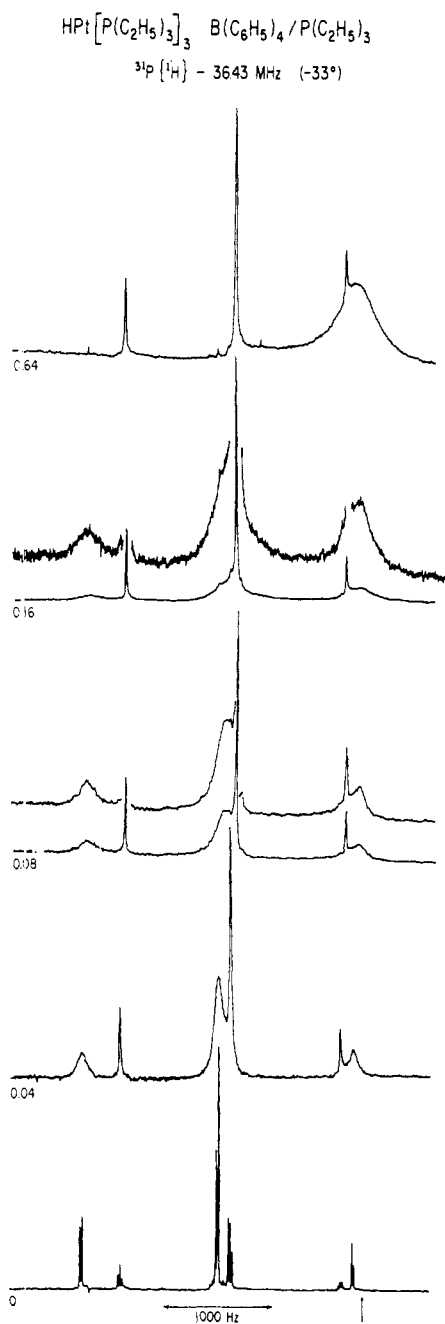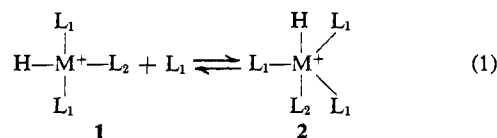
HPt[P(C$_2$H$_5$)$_3$]$_3$ B(C$_6$H$_5$)$_4$/P(C$_2$H$_5$)$_3$

³¹P {¹H} - 3643 MHz (-33°)

Figure 1. The 36.43-MHz Fourier mode proton decoupled ³¹P nmr spectrum for a 0.17 M solution of HPt[P(C$_2$H$_5$)$_3$]$_3$$^+$B(C$_6H_5$)$_4$$^-$ in acetone as a function of added ligand concentration at −33°. The number beneath the spectra is the added ligand concentration (mol l.$^{-1}$) and the arrow indicates the resonance frequency of the free ligand.

scrambling of L$_2$ with the L$_1$ ligands. Also, it is clear that on the average the Pt–L$_2$ bond is not broken (both the HP$_2$ and P$_2$Pt couplings are retained). The increase

in exchange rate with added ligand signifies that the exchange process is associative with the mechanism shown below[3-5]

$$H-\overset{\overset{\displaystyle L_1}{|}}{\underset{\underset{\displaystyle L_1}{|}}{M^+}}-L_2 + L_1 \rightleftharpoons L_1-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle L_2}{|}}{M^+}}\overset{L_1}{\underset{L_1}{}} \qquad (1)$$

$$\quad\quad\quad\quad\quad 1 \quad\quad\quad\quad\quad\quad 2$$

All of the spectral features shown in Figure 1 can be rationalized in terms of eq 1 together with the assumption that the concentration of **2** remains low even at high ligand concentrations. (If the concentration of **2** becomes large the resonances assigned to L$_2$ would broaden because of averaging of the L$_2$ environments in **1** and **2**.)

Similar ³¹P line shape effects are found by studying the temperature dependence of the ³¹P{¹H} spectrum for a solution of HPt[P(C$_2$H$_5$)$_3$]$_3$$^+$B(C$_6H_5$)$_4$$^-$ in the presence of added ligand (0.08 mol l.$^{-1}$). The relatively small temperature dependence of the nmr line shapes implies a large (negative) entropy of activation in accord with the postulated associative process.

The nmr line shape behavior for HPd[P(C$_2$H$_5$)$_3$]$_3$$^+$-B(C$_6H_5$)$_4$$^-$,[6] although basically similar, shows significant differences from that of the corresponding Pt complex; the ³¹P{¹H} nmr spectrum is an A$_2$B pattern. The hydride region ¹H nmr spectrum is a doublet, since the HP$_1$ coupling in this case is genuinely small (~0) and there is no exchange decoupling (the ³¹P nmr spectrum is a sharp A$_2$B pattern). On addition of small concentrations of P(C$_2$H$_5$)$_3$ to the solution, resonances assigned to the A phosphorus nuclei (L$_1$) in the ³¹P{¹H} nmr spectrum broaden much more rapidly than those assigned to the B resonances and the hydride region ¹H nmr spectrum is almost unaltered. However, at higher ligand concentrations and temperatures all the resonances in the ³¹P nmr spectrum collapse into a single broad line; the doublet observed in the hydride region ¹H nmr spectrum is exchange decoupled into a broad singlet. These line shape effects can again be interpreted in terms of eq 1 with the additional assumption that the *intramolecular rearrangement of* **2** *is significant*. The nmr line shapes do qualitatively show that the dissociative process involving loss of one of the equatorial ligands in **2** is faster than the intramolecular rearrangement at all temperatures in the range −90 to +35°.

The Fourier mode ³¹P{¹H} nmr spectrum of a solution of HNi[P(C$_2$H$_5$)$_3$]$_3$$^+$B(C$_6H_5$)$_4$$^-$ [6] is also an A$_2$B

(3) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.
(4) (a) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 92, 4996 (1970); (b) P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969).
(5) D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 95, 1102 (1973).
(6) R. A. Schunn, to be submitted for publication.

spectrum at low temperatures. The hydride region ^{1}H nmr spectrum is the X part of an A_2BX pattern and suggests that $HNi[P(C_2H_5)_3]_3^+$ at first undergoes a *mutual intramolecular exchange process* as the temperature is raised. (The two intense inner lines in the spectrum remain sharp as the rest of the spectrum broadens.) On further raising the temperature the spectrum collapses to a singlet due to intermolecular exchange. The associative nature of the latter process is revealed by the fact that addition of $P(C_2H_5)_3$ induces the collapse to a singlet at much lower temperatures. These line shape changes can again be rationalized in terms of eq 1, but now *the five-coordinate intermediate* **2** *must undergo intramolecular exchange more rapidly than it loses a ligand in a dissociative process*. These trends are in accord with our earlier observation that in d^8 HML_4 complexes the barriers to mutual exchange increase with increasing atomic number.[7]

Nmr line shape analyses are being carried out to obtain quantitative data for these systems. It is clear, however, from the qualitative data presented that this type of study can give insight into ligand exchange processes, rearrangements in transition states (or reaction intermediates), and the relative rates of cis-trans isomerization *vs.* intermolecular exchange to a degree not readily achieved by other approaches.

(7) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

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Inductive Effect of a Carbonyl Group. The Electronic Structure of [5]Annulenones[1]

Sir:

In a recent publication[2] dealing with the photoelectron (pe) spectra of cyclopent-2-enone (**2**) and cyclopent-3-enone (**3**), a conjugative interaction between the $\pi_{C=C}$ MO and the vacant $\pi^*_{C=O}$ was postulated.[3] As a consequence the $\pi_{C=C}$ MO is stabilized relative to cyclopentene. By means of the pe spectra of 2,5-di-*tert*-butylcyclopentadienone[4] (**5**) and 3,4-di-*tert*-butyl-

(1) Part 27 of "Theory and Application of Photoelectron spectroscopy;" part 26: H. Schmidt and A. Schweig, *Tetrahedron Lett.*, 1437 (1973).

(2) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93**, 4320 (1971).

(3) The theoretical reasoning throughout this work is based on the localized MO method. Considering the π MOs only two sorts of interaction between the ethylene (or *cis*-butadiene) and carbonyl moieties must be taken into account: (i) the inductive effect (field effect and polarization of the σ electrons) exerted by the charge polarized carbonyl group (due to its σ and π electrons) on the ethylene (or *cis*-butadiene) π MOs and (ii) the conjugative interaction between all occupied and vacant π MOs (as modified by effect i) of both systems.

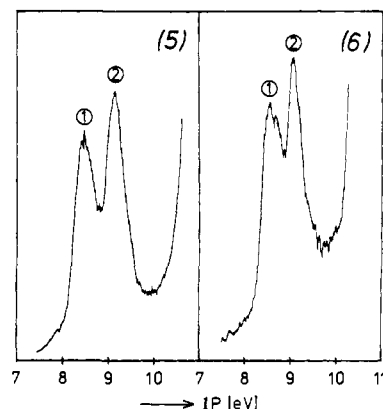(4) G. Maier and F. Bosslet, *Tetrahedron Lett.*, 1025 (1972).

Figure 1. Sections of the photoelectron spectra of 2,5-di-*tert*-butylcyclopentadienone (**5**) and 3,4-di-*tert*-butylcyclopentadienone (**6**). The measured vertical ionization potentials [eV] are: for (**5**) 1, 8.50; 2, 9.15; for (**6**) 1, 8.60; 2, 9.10. The He-I (584 Å) photoelectron spectra were recorded on a PS-18 spectrometer from Perkin-Elmer, Beaconsfield (England).

cyclopentadienone[5] (**6**), we are now able to explain the observed stabilization of the π MO by the inductive effect of the C=O group.[3]

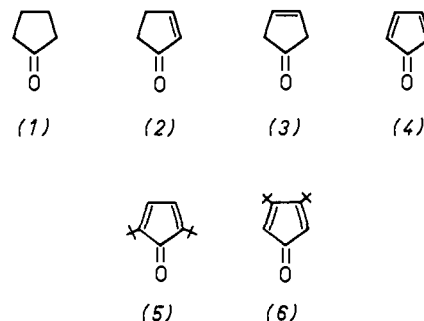Figure 1 shows sections of the pe spectra of **5** and **6**. Both spectra exhibit two bands at nearly the same position below the σ continuum. Band 2 (**5**, 9.15 eV; **6**, 9.10 eV) must be assigned to ionization from the oxygen lone pair,[6] the corresponding lone pair ionizations (IPs) of **1**, **2**, and **3** are, for comparison, (**1**) 9.25 eV,[2] (**2**) 9.34 eV,[2] and (**3**) 9.44 eV.[2] Band 1 (**5**, 8.50 eV; **6**, 8.60 eV) then is due to ionization from the π (a_2) MO (node along the C=O bond; *cf.* the representation of this MO).
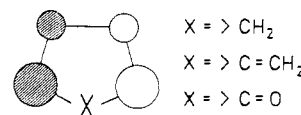
The $\pi(a_2)$ HOMOs ("highest occupied MOs") of cyclopentadiene (8.57 eV[7]) and fulvene (8.55 eV[8]) have the same symmetry and topology as the HOMO in cyclopentadienone (**4**). On introducing two *tert*-butyl

(5) G. Maier, G. Fritschi, and R. Hoppe, *Angew. Chem.*, **82**, 551 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 529 (1970).

(6) The determination of MO energies throughout this work is based on the validity of Koopmans' theorem: T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).

(7) P. J. Derrik, L. Asbrink, O. Edquist, B. O. Jonsson, and E. Lindholm, *Int. J. Mass. Spectrom. Ion Phys.*, **6**, 203 (1971).

(8) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971).