philic attack, presumably at the acyl carbon, to give **5**.[5]

3. **β-Hydride Elimination.** The β elimination of Pd–H from alkyl–Pd intermediates in catalytic and other reactions has been a frequently postulated process,[13] but definitive evidence for this reaction has hitherto been lacking. We now find that β elimination of Pd–H occurs when **1** is reacted with triphenylphosphine.

Treatment of **1** with 2 equiv of PPh_3 (per Pd) in $CDCl_3$ under an argon atmosphere gave α-(pentamethylcyclopentadienyl)styrene (**6**)[14] and a clear solution, the nmr of which showed the presence of a high-field hydrogen (at τ 24.8) which we assign to $(Ph_3P)_2PdHCl$.[15] The solution was relatively stable ($t_{1/2}$ *ca.* 18 hr at 25°) but on exposure to air the hydride signal disappeared and $(Ph_3P)_2PdCl_2$ was slowly precipitated. The latter complex and **6** were formed directly when the reaction was carried out in CCl_4 and in that case chloroform was detected by nmr. Full details of these and other reactions will be reported shortly.

Acknowledgment. We thank the National Research Council of Canada for support.

(13) Reference 2, pp 93–95; ref 1, pp 9–16; and, for example, R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, 5538 (1968).

(14) **6**: colorless oil; nmr δ 1.12 (s, 1 Me), 1.64 (m, 4 overlapping Me's), 5.17 (d, J = 1.5 Hz, 1 H), 5.26 (d, 1 H), and 7.05 (m, phenyl).

(15) This complex was recently reported[16] but no nmr data were given.

(16) K. Kudo, M. Hidai, T. Murayama, and Y. Uchida, *Chem. Commun.*, 1701 (1969).

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The Nature of Chlorotris(triphenylphosphine)rhodium in Solution and Its Reaction with Hydrogen

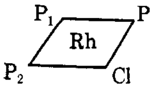
Sir:

Solutions of $RhCl[P(C_6H_5)_3]_3$ are among the most efficient hydrogenation catalysts yet discovered and have occupied a central role in the development of modern homogeneous catalysis. Since the classic first paper of Wilkinson and coworkers[1] there has been a large number of contributions dealing with catalysis using this complex, none of which has questioned several basic features of the mechanism originally proposed.[1] It has been assumed that the first step involves ligand dissociation from the parent complex followed, under most conditions, by addition of molecular hydrogen, coordination of the olefin, and elimination of the hydrogenated product. In the initial publication,[1] molecular weight measurements were interpreted in terms of complete dissociation according to eq 1;

$$RhCl[P(C_6H_5)_3]_3 \xrightleftharpoons{K_1} RhCl[P(C_6H_5)_3]_2 + P(C_6H_5)_3 \qquad (1)$$

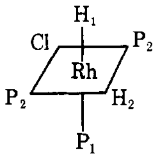
subsequent publications[2-4] have suggested that the degree of dissociation is, in fact, much smaller.

$RhCl[P(C_6H_5)_3]_3$ (configuration **1**) is readily detected in solution using ^{31}P nmr.[2,5] We have repeated the measurements to establish, for our spectrophotometric studies, that the trisphosphine species is the major component in solution. The ^{31}P proton noise decoupled nmr spectrum for **1** is shown in the first line of Figure 1; the spectrum is unaffected by the addition of excess triphenylphosphine at 30°, and a new resonance appears in the position of free ligand. Similar results were obtained using the more soluble complex RhCl[P(p-tolyl)$_3$]$_3$. We did not detect free $P(C_6H_5)_3$ (expected at the position of the arrow in Figure 1) in the cw spectrum of $RhCl[P(C_6H_5)_3]_3$. However, by using the Fourier transform nmr technique we were able to detect a weak free phosphine resonance in a solution of 0.05 M complex in CH_2Cl_2 with an intensity about 3% of that of the principal species.



1

Addition of molecular H_2 to a solution of $RhCl[P(C_6H_5)_3]_3$ forms a dihydride which is readily detected in the proton nmr.[1] ^1H nmr spectra for the hydride region at two temperatures are shown in Figure 2; the spectra show well-resolved fine structure at −25° and broadening above room temperature due to phosphorus ligand exchange. Similarly the ^{31}P nmr spectra with proton noise decoupling are shown for the hydride species at two temperatures in part B of Figure 1. It is clear from the spectrum at −25° that the hydride species is formed almost quantitatively and that it contains three phosphorus ligands. The structure may be unambiguously assigned as configuration **2**. Part C of Figure 1 shows that the equilibrium may be reversed by passing N_2 through the solution. No resonance for free triphenylphosphine was observed in these cw spectra.



2

From the spectrum in Figure 1B at 30° it is clear that phosphorus ligand dissociation is proceeding at an appreciable rate. Since the P_2–Rh coupling is preserved while the P_1–Rh and P_1–P_2 couplings are removed, we can deduce that under these conditions only the P_1 phosphorus (the one trans to H_1 in **2**) is dissociating and that it returns to the coordination site from which it left. Preliminary line-shape studies give an approximate rate constant k_2 for the forward step of reaction 2 of $\sim$400 sec^{-1} at 30°. This, coupled with the absence of line-shape effects associated with the phosphorus atoms P_2 (configuration **2**), suggests a rather small degree of dissociation for the six-coordinate species. Thus it appears that the five-coordinate hydrides de-

$$RhH_2Cl[P(C_6H_5)_3]_3 \xrightleftharpoons{K_2} RhH_2Cl[P(C_6H_5)_3]_2 + P(C_6H_5)_3 \qquad (2)$$

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(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966)

(2) D. R. Eaton and S. R. Suart, *J. Amer. Chem. Soc.*, **90**, 4170 (1968).

(3) D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Commun.*, 1486 (1970).

(4) H. Arai and J. Halpern, *ibid.*, 1571 (1971).

(5) T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, **92**, 2359 (1970).

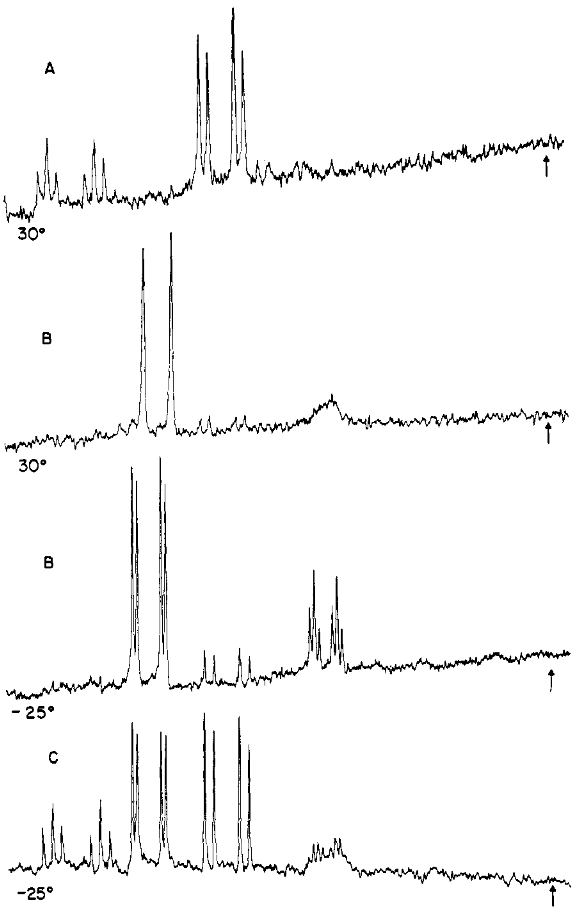

Figure 1. (A) 36.4-MHz ^{31}P proton noise decoupled spectrum for 0.14 M solution of $RhCl[P(C_6H_5)_3]_3$ in CH_2Cl_2. The nmr parameters are $\delta P_1 = -48.94$; $\delta P_2 = -32.21$; $J_{P_1P_2} = 37.5$ Hz; $J_{P_1Rh} = 192$ Hz and $J_{P_2Rh} = 146$ Hz with the nuclear labeling scheme shown in configuration **1**; chemical shifts are in parts per million relative to external 80% H_3PO_4, negative values being to low field. (B) Spectrum at two temperatures after addition of molecular hydrogen to solution A. The spectral parameters for $RhH_2Cl[P(C_6H_5)_3]_3$ obtained in conjunction with the data from Figure 2 are $\delta H_1 = 9.75$ ppm; $\delta H_2 = 17.33$ ppm; $J_{H_1P_1} = 152$ Hz; $\delta P_1 = -20.68$ ppm; $\delta P_2 = -40.30$ ppm; $J_{P_1P_2} = 17.5$ Hz; $J_{P_1Rh} = 90$ Hz; $J_{P_2Rh} = 114$ Hz with the nuclear labeling scheme shown in configuration **2**. The remaining five coupling constants are probably <10 Hz. Proton chemical shifts are given in parts per million relative to TMS. (C) Spectrum after sweeping nitrogen through the solution.

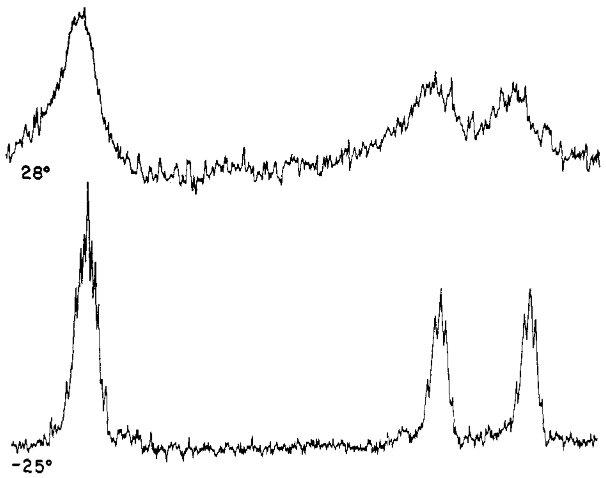

Figure 2. 90-MHz ^1H spectrum of hydride region for CH_2Cl_2 solution of $RhH_2Cl[P(C_6H_5)_3]_3$ at two temperatures.

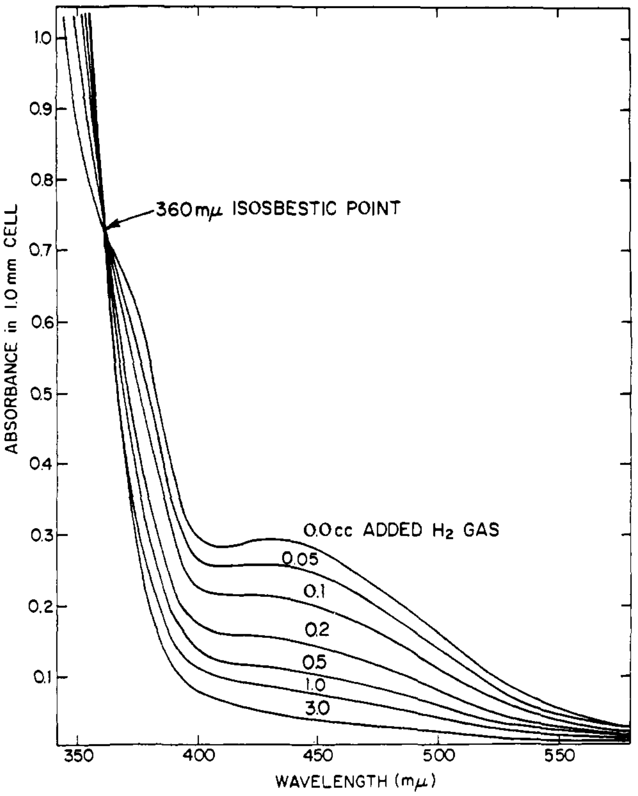

Figure 3. Uv spectrum of CH_2Cl_2 solution of 2.31×10^{-3} M $RhCl[P(C_6H_5)_3]_3 + 0.1$ M $P(C_6H_5)_3$ in 1.0-mm cell at 26° with successive addition of hydrogen to 2 cc of liquid.

scribed in ref 1 are really six coordinate and similar to those in ref 6 and 7.

Spectrophotometric studies of the system $RhCl[P(C_6H_5)_3]_3$ and H_2 in CH_2Cl_2 containing added $P(C_6H_5)_3$ show a clear isosbestic point at 360 mμ, indicating the presence of only two chromophoric species and, on the basis of the nmr data given above, these must correspond to equilibrium 3. Figure 3 shows the

$$H_2 + RhCl[P(C_6H_5)_3]_3 \overset{K_3}{\rightleftharpoons} RhH_2Cl[P(C_6H_5)_3]_3 \qquad (3)$$

uv spectra obtained by adding increasing amounts of H_2 to a solution containing $RhCl[P(C_6H_5)_3]_3$ and excess triphenylphosphine; an equilibrium constant $K_3 = 4.7 \pm 0.8 \times 10^3$ M^{-1} is derived from these data assuming a solubility of 0.05 cc H_2/cc CH_2Cl_2 at 25°. Similar behavior was obtained in the absence of added triphenylphosphine and in studies carried out in benzene instead of CH_2Cl_2.

Dissociation of $P(C_6H_5)_3$ from $RhCl[P(C_6H_5)_3]_3$ according to eq 1 with $K_1 = 1.4 \times 10^{-4}$ M has recently been suggested on the basis of spectrophotometric experiments on dilute benzene solutions.[4] We have repeated these experiments and find that $RhCl[P(p\text{-tolyl})_3]_3$ behaves similarly. While it is clear that phosphine dissociation occurs in dilute solutions, we prefer to ascribe effects of added L and deviations from Beer's law to eq 4, based on studies on the soluble dimer

$$2RhClL_3 \overset{K_4}{\rightleftharpoons} [RhClL_2]_2 + 2L \qquad (4)$$

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(6) A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. A*, 1670 (1966).

(7) J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, **46**, 60 (1968).

with L = P(p-tolyl)$_3$, where $K_4 \sim 4 \times 10^{-4}\ M$ in benzene at 25°. The dimer obeys Beer's law and has a ^{31}P spectrum consisting of a non-first-order doublet of triplets. The large doublet splitting is assigned to J_{PRh} while the small triplet splitting may be due to $J_{\mathrm{PRh}Rh}$ or J_{PRhRhP}; in any event the spectrum is inconsistent with a monomeric species RhClL$_2$. In the presence of 0.01 M or higher added L, solutions of RhClL$_3$ complexes do obey Beer's law, showing that equilibrium 4 is forced to the left under these conditions. There was no evidence for RhClL$_4$ formation even in 0.5 M L.

Our studies show that RhCl[P(C$_6$H$_5$)$_3$]$_3$ and RhH$_2$Cl[P(C$_6$H$_5$)$_3$]$_3$ are the major species present in solutions of tris(triphenylphosphine)rhodium chloride and hydrogen. Reactions 3 and 2 represent the first two steps in the "hydride" route[1,7] to hydrogenation, the subsequent step presumably being coordination of the olefin to the site vacated by P$_1$. This mechanism is in harmony with the basic postulate that, in general, only 16- and 18-electron complexes are present in homogeneous reactions catalyzed by group VIII transition metal complexes, other species being energetically unfavorable.[8] A similar sequence of reactions obeying this rule can be written for the "unsaturate" route.[1,7] Detailed studies of various other aspects of the olefin hydrogenation system are currently being investigated.

Acknowledgment. We are indebted to Professor J. H. Noggle of the University of Delaware for the use of their Bruker HFX-90 spectrometer in obtaining Fourier transform ^{31}P spectra on dilute solutions of RhCl[P(C$_6$H$_5$)$_3$]$_3$, to G. Watunya for obtaining the cw spectra in Figures 1 and 2 on a similar spectrometer, and to D. W. Reutter for the Cary 14 spectra.

(8) C. A. Tolman, accepted for publication in *Quart. Rev., Chem. Soc.*

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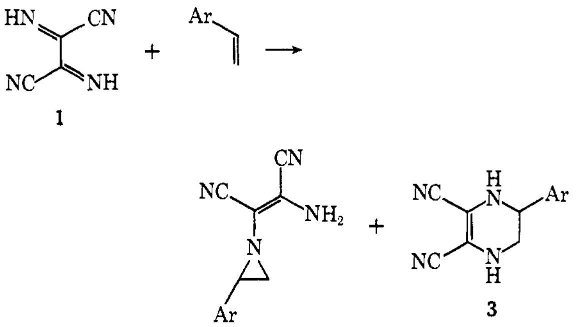
Hydrogen Cyanide Chemistry. II. Reactions of Diiminosuccinonitrile with Olefins

Sir:

Diiminosuccinonitrile (DISN), prepared by base-catalyzed addition of hydrogen cyanide to cyanogen, has been found to be a highly reactive and versatile intermediate, particularly valuable in the synthesis of new heterocycles through condensation and displacement reactions.[1] We now wish to report that the 1,4-diazabutadiene (HN=C—C=NH) system[2] of this polyfunctional reagent behaves like a zwitterionic nitrenium ion toward sufficiently nucleophilic olefins and furthermore the reaction products depend highly on the electronic character of the olefin substituents.

Styrene and p-halostyrenes reacted with DISN in acetonitrile at room temperature to give 2-amino-3-(2-arylaziridin-1-yl)maleonitrile (**2a–c**) in 50–80% yield,[3,4] whereas the more electron-rich p-methoxystyrene and 2-vinylfuran gave 5-aryl-2,3-dicyano-1,4,5,6-tetrahydropyrazine (**3e** and **3f**) in 60–80% yield.[3,5] While in the latter cases the reaction was complete within a day and no aziridine could be detected; DISN was still present in the former reactions even after several days, but no tetrahydropyrazine was detected in the reaction mixture. p-Methylstyrene gave both types of products, **2d** and **3d** (eq 1).



1

2 **3**

(1)

yield, %[3]

	2	3
a, Ar = C$_6$H$_5$	58	
b, Ar = p-ClC$_6$H$_4$	51	
c, Ar = p-FC$_6$H$_4$	79	
d, Ar = p-CH$_3$C$_6$H$_4$	62	1.3
e, Ar = p-CH$_3$OC$_6$H$_4$		60
f, Ar = 2-furyl		81

That the aziridine formation proceeds with retention (>98%) of olefin stereochemistry was demonstrated by the reaction of cis- and $trans$-β-methylstyrene[6] with DISN. It was previously reported[1] that the cycloaddition of cis-1,2-dimethoxyethylene with DISN to 2,3-dicyano-5,6-dimethoxy-1,4,5,6-tetrahydropyrazine also occurs with retention of stereochemistry.

Mechanistically, we postulate that DISN interacts with sufficiently nucleophilic olefins in such a manner that the 1,4-diazabutadiene is progressively polarized to a zwitterionic nitrenium ion (see **5**) as the transition state is approached. This novel polarization is probably assisted by generation of the highly resonance stabilized dicyanovinylamide ion. Since nitrenium ions[7] are isoelectronic with carbenes, **5** is expected to give zwitterionic aziridinium ion **4**[8] with retention of olefin stereochemistry (eq 2). Migration of a hydrogen atom from the ring nitrogen to the amido nitrogen

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(1) R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.*, **93**, 4953 (1971).

(2) The system has been virtually unknown and very little studied; see G. Tuchtenhagen and K. Rühlman, *Justus Liebigs Ann. Chem.*, 711, 174 (1968).

(3) All reactions were carried out in acetonitrile in the presence of excess olefins at room temperatures except where noted otherwise. The yields are not optimized. All new compounds gave correct elemental analyses and consistent spectral (iv, uv, nmr) data.

(4) Typically, **2a** showed uv$_{\max}$ (C$_2$H$_5$OH) 300 nm (ϵ 14,200); nmr (CDCl$_3$) δ 2.50 (d, 1, J = 4 Hz, $trans$-CH$_2$), 2.66 (d, 1, J = 7 Hz, cis-CH$_2$), 3.12 (d of d, 1, J = 4, 7 Hz, CH), 4.55 (br, 2, NH$_2$), 7.33 (s, 5, arom).

(5) Typically, **3e** showed uv$_{\max}$ (C$_2$H$_5$OH) 324 nm (ϵ 10,300), 224 (21,800); nmr (CD$_3$CN–D$_2$O) δ 2.96 (d of d, 1, J = 12.5, 6.6 Hz, $trans$-CH$_2$), 3.38 (d of d, 1, J = 12.5, 3.2 Hz, cis-CH$_2$), 4.11 (d of d, 1, J = 6.6, 3.2 Hz, CH), 3.81 (s, 3, OCH$_3$), 7.11 (AB, 4, arom). The tetrahydropyrazines (**3**) are readily converted to the corresponding 5-aryl-2,3-dicyanopyrazines.

(6) The reaction of cis-β-methylstyrene required reflux in acetonitrile.

(7) Nitrenium ions have been shown to add to double bonds: P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970); also see W. Nagata, S. Hirai, K. Kawata, and T. Aoki, *J. Amer. Chem. Soc.*, **89**, 5045 (1967).

(8) Although DISN is believed to be transoid,[1] **4** is assumed to possess a maleonitrile side chain. It is not clear how and when this isomerization occurs; however, DISN is readily converted to diaminomaleonitrile (DAMN) derivatives in many reactions[1] and DAMN is thermodynamically more stable than diaminofumaronitrile: Y. Yamada, N. Nagashima, A. Nakamura, and I. Kumashiro, *Tetrahedron Lett.*, 4529 (1968).