of azide and cooling of the mixture to 4 °C. From the known rate of reduction, the amount of deoxyHr was close to 10% in the 0.7-h sample of [semi-met(N_3)] used for spectral measurement (Figure 4). The sample for the 0.4-h spectrum of [semi-met(OH)] (Figure 4) was maintained at ~4 °C from the time of addition of dithionite and, thus, contained only 3% deoxyHr. The amount of unreduced metHr(N_3) and metHr(OH) as judged by remaining intensity at 680 and 610 nm, respectively, was 2% for the 0.7-h sample of [semi-met(N_3)] and 5% for the 0.4-h sample of [semi-met(OH)].

The half-reduced forms are characterized by shifts in the Fe(III) LF bands from 680 nm in metHr(N_3) to 730 nm in [semi-met(N_3)] and from 480 and 610 nm in metHr(OH) to 490 and 670 nm, respectively, in [semi-met(OH)] (Table I). The near-IR spectrum of [semi-met(OH)] probably contains an Fe(II) component at ~850 nm in addition to the distinct Fe(III) component at 995 nm (Figure 4). In the [semi-met(N_3)] spectrum near-IR peaks are clearly observed at 910 and 1190 nm (Figure 4). The presence of the latter two spectral features is entirely consistent with formulation of the binuclear iron unit in [semi-met(N_3)] as a class II[17] mixed-valence system. The 910-nm band very likely includes contributions both from Fe(II) and Fe(III) transitions. The broad 1190-nm absorption ($\Delta\bar{\nu}_{1/2}$ = 4000 cm^{-1}; ϵ = 16 M^{-1} cm^{-1}) is probably derived from Fe(II) LF excitation, with a degree of electron delocalization (intervalence character) in the [Fe(II)*, Fe(III)] excited state as a possible explanation for the enhanced intensity.[18]

In addition to the 1190 nm [Fe(II)*,Fe(III)] band observed for [semi-met(N_3)], both [semi-met(N_3)] and [semi-met(OH)] exhibit low-temperature EPR signals typical of an $S = {}^1/_2$ [Fe(II),Fe(III)] system,[19] presumably arising from the spin-spin interaction of $S = 2$ Fe(II) and $S = {}^5/_2$ Fe(III) ions. However, an [Fe(II)*,Fe(III)] band was not detected in the near-IR spectrum of [semi-met(OH)]. Clearly, N_3^- plays an important role in enhancing the [Fe(II)*,Fe(III)] band intensity in [semi-met(N_3)]; the structural implications of this finding, however, remain to be elucidated.

Conclusions

The electronic spectra of methemerythrin, oxyhemerythrin, and semi-methemerythrin have ligand field bands characteristic of octahedral Fe(III) complexes while the electronic spectrum of deoxyhemerythrin is typical of octahedral Fe(II) species. The two iron atoms in hemerythrin can, therefore, by unequivocally assigned to octahedral symmetry in all three oxidation states of the protein. Among the best models for the iron sites in hemerythrin are the iron-EDTA complexes, which share the property of having similar numbers of N and O ligands.

Acknowledgment. We are grateful to Dr. Patricia C. Harrington and Dr. Vincent Miskowski for many helpful discussions. This research was supported by grants from the National Science Foundation (Grant CHE 77-11389) and the National Institutes of Health (Grant GM 18865).

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(17) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247-405.

(18) Smith, G. *Phys. Chem. Miner.* **1978**, *3*, 375-383.

(19) Muhoberac, B. B.; Wharton, D. C.; Babcock, L. M., Department of Biochemistry, University of Texas Health Science Center, and Harrington, P. C.; Wilkins, R. G., Department of Chemistry, New Mexico State University, 1980, personal communication.

Synthesis, Structures, Stabilities, and Reactions of Cationic Olefin Complexes of Palladium(II) Containing the η^5-Cyclopentadienyl Ligand[1]

Hideo Kurosawa,* Tetsuro Majima, and Naonori Asada

Contribution from the Department of Petroleum Chemistry, Osaka University, Suita, Osaka 565, Japan. *Received January 2, 1980*

Abstract: Syntheses of various cationic olefin complexes of palladium(II), [Pd(η^5-C_5H_5)(PR_3)(olefin)]X (R = Ph, Et, *n*-Bu; X = ClO_4, BF_4), **4**, a class of compounds much more stable than hitherto known, are reported. **4** exhibited ^{1}H and ^{13}C NMR spectral aspects remarkably well-defined for an olefin-palladium complex, providing means of studying configurations and relative stabilities in some detail. In **4** containing substituted styrenes, ^{13}C NMR shifts of the olefin carbons correlate with the Hammett σ^+ parameters, while stabilities of the complexes correlate better with σ than σ^+. A possible significance of ion pair formation in determining stability trends has been suggested. Olefin ligands rotate more rapidly about the palladium-olefin axis than the platinum-olefin axis. This result, as well as a different substituent dependency of the stability in series of substituted styrene complexes of palladium(II) and platinum(II), is explained in terms of less effective π back-bonding from palladium to olefin than from platinum. The ethylene complex of type **4** reacts with some nucleophiles to give alkyl complexes, Pd(η^5-C_5H_5)(PPh_3)(CH_2CH_2Y) [Y = CH(COMe)$_2$ **9**, OR **10**], a class of compounds again remarkably stable for a substituted ethylpalladium(II) complex. ^{1}H NMR spectra of **9** and **10** prepared from the *cis*- and *trans*-ethylene-d_2 complexes indicated the trans addition of Pd and Y to ethylene. **9** and **10** undergo thermolysis via β-hydrogen elimination which is suggested to proceed through predissociation of PPh_3. The role of the η^5-C_5H_5 ligand in raising stabilities of olefin and alkyl complexes of palladium(II) has been discussed in the light of the data.

A wide variety of synthetic reactions mediated by palladium utilize olefin-palladium(II) complexes as starting materials or as crucial intermediates.[2] Nevertheless, in contrast to extensive olefin-platinum(II) chemistry, a rather limited number of studies have been reported on olefin complexes of palladium(II) with a particular emphasis on the nature of the metal-olefin bond or reactivities bearing on elementary steps involved in the synthetic reactions. This is clearly attributed, in part, to rather a labile character of the bond between palladium(II) and olefins, especially simple monoolefins whose complexes might lack such extra stabilization as is found in chelate complexes of diolefins or olefins containing donor atoms.[3] Studies using simple monoolefins appear

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(1) Part of this work has been presented at the ACS-CSJ Chemical Congress, April, 1979, Honolulu, Hawaii, Inor. 227.

(2) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 2.

(3) Reference 2, Vol 1, pp 106.

0002-7863/80/1502-6996$01.00/0

Table I. Properties of $[Pd(C_5H_5)(PR^1{}_3)(CH_2{=}CHR^2)]X^a$

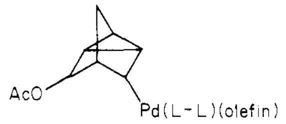
no.	X	R^1	R^2	color	mp,^{b} °C
4a	ClO_4	C_6H_5	H	violet	156
4b	ClO_4	C_6H_5	CH_3	violet	145
4c^c	ClO_4	C_6H_5	*p*-ClC_6H_4	dark-green	107
4d	ClO_4	C_6H_5	C_6H_5	blue	113
4e^c	ClO_4	C_6H_5	*p*-$CH_3C_6H_4$	dark-green	152–153
4f^c	ClO_4	C_6H_5	*p*-$CH_3OC_6H_4$	green	147–149
4g	ClO_4	C_2H_5	C_6H_5	violet	120
4h	ClO_4	*n*-C_4H_9	*p*-$NO_2C_6H_4$	dark-violet	112–115
4i	ClO_4	*n*-C_4H_9	*p*-$CH_3COC_6H_4$	dark-violet	105
4j	ClO_4	*n*-C_4H_9	*p*-ClC_6H_4	violet	101–103
4k	ClO_4	*n*-C_4H_9	C_6H_5	violet	94
4l	ClO_4	*n*-C_4H_9	*p*-$CH_3C_6H_4$	red-violet	95–97
4m	ClO_4	*n*-C_4H_9	*p*-$CH_3OC_6H_4$	violet	108
4n	BF_4	*n*-C_4H_9	*p*-ClC_6H_4	red-violet	100–102
4o	BF_4	*n*-C_4H_9	C_6H_5	violet	72–74
4p	BF_4	*n*-C_4H_9	*p*-$CH_3OC_6H_4$	red-violet	118

^{a} All the compounds gave satisfactory analytical results (C and H, and N, if contained). ^{b} With decomposition. ^{c} CH_2Cl_2 solvate (also confirmed by ^1H NMR).

to have some advantages over chelating olefins, e.g., ease of resolving spectral features or accessibility of a series of systematically substituted substrates. Most of isolable monoolefin complexes of palladium(II) reported until now are the Kharash-type compounds,[3] $[PdCl_2(olefin)]_2$, but stabilities of these complexes in solutions are not sufficiently high for studying solution chemistry bearing on configurational, thermodynamic, and kinetic aspects of the complexes. On the other hand, some significant contributions were made, without isolating any representative compound, to a comparative study in aqueous solutions or organic solvents on thermodynamics of monoolefin complexes of palladium(II) which are either negatively charged[4] (**1**) or electrically neutral[5,6] (**2**, **3**). No related work has been reported, however, of cationic olefin–palladium(II) complexes. We reported recently[7] that lability of the palladium–olefin bond in a cationic complex, both in the solid state and in solutions, can be diminished to a great extent by adopting the η^5-cyclopentadienyl group (Cp) as an ancillary ligand (**4**). This finding has now opened a way for palladium to become a new member of those metals of which cationic Cp complexes containing olefinic ligands have received much attention in the last few years[8] from various viewpoints including the nature of metal–olefin bond and reactivity. We describe here synthesis, structures, stabilities, and reactions of such a class of olefin complexes of palladium(II). By use of one of these complexes, valuable information has already been provided[9,10] concerning the stereochemistry of nucleophilic attack on the olefins coordinated to palladium.

$[PdCl_3(olefin)]^-$

1



2, L–L = $CH(COCF_3)_2$, $CH(COCF_3)(COPh)$

$PdCl_2(py)(olefin)$

3

$[Pd(\eta^5\text{-}C_5H_5)(PR_3)(olefin)]X$

4

$[M(\eta^5\text{-}C_5H_5)(PPh_3)(CO)]ClO_4$

5, M = Pd
7, M = Pt

Results and Discussion

Synthesis and NMR Spectra of Olefin–Palladium(II) Complex. The complexes **4a–p** listed in Table I could be isolated as crystalline solids from eq 1. The formation in solutions of other olefin

$$Pd(\eta^5\text{-}C_5H_5)(PR_3)(Br) \xrightarrow[AgX]{olefin} \mathbf{4} + AgBr \qquad (1)$$

complexes, examined in the relative stability study discussed later through ligand exchange using the nitrile complexes or those in Table I (eq 2), was unambiguously confirmed by characteristic

$$[Pd(\eta^5\text{-}C_5H_5)(PR_3)(L)]X + olefin \rightleftharpoons [Pd(\eta^5\text{-}C_5H_5)(PR_3)(olefin)]X + L \qquad (2)$$

$L = C_6H_5CN$, *o*-$C_6H_4(CH_3)CN$, olefin different from addend

NMR spectra (for typical examples, see **4q–t** in Table II). However, these complexes could not be isolated by eq 1 due to difficulty in crystallization. There seems to exist no direct relation between the stability of the complexes and a possibility of isolating these as solid samples. Most of the complexes thus formed were stable at ambient temperature in concentrated acetone or chloroform solutions for an order of days but decomposed rapidly when heated at above 50 °C. Among the products identified after the styrene complex **4d** was decomposed in solutions are $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)_2]ClO_4$ and the styrene dimer, *trans*-1,3-diphenyl-1-butene. This dimer formation took place catalytically with respect to the palladium complex if a large excess of styrene was added to the solution of **4d** prior to decomposition.

The carbonyl complex, $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CO)]ClO_4$ (**5**), which is again much more stable than the known 4-coordinate palladium–carbonyl complexes,[11] was obtained in a manner similar to eq 1. Attempts to prepare the organoplatinum(II) analogues of **4** and **5** have so far been unsuccessful except for $[Pt(\eta^5\text{-}C_5H_5)(PPh_3)(L)]ClO_4$ (**6**) ($L = CH_2{=}CH_2$) and **7** (L = CO), partly due to difficulty in crystallization and partly due to a limited availability of compounds of type $Pt(\eta^5\text{-}C_5H_5)(PR_3)(Br)$.[12] No ligand-exchange reaction similar to eq 2 could be found to occur in the case of **6**.

Very few workers have previously reported well-defined NMR spectra of olefin–palladium(II) complexes. The ^1H and ^{13}C NMR spectra of the class of complexes investigated in this work (Tables II and III) are characterized by (1) sharp lines for most of the olefinic proton resonances, (2) observation of separate sets of resonances due to the coordinated and free olefins when the solution contains an equilibrium mixture expressed by eq 2, and (3) the large magnitudes of the up-field shift of the coordinated olefin protons as well as the carbon resonances relative to those of free olefins.[13] These advantageous spectral features made it easy to examine configurations and relative stability of the olefin–palladium complexes in some detail (see later).

Observation 2 described above indicates that rates of exchange of coordinated with free olefins are much slower than the NMR time scale even at 23 °C. In contrast to this, the spectra of all the known olefin–palladium(II) complexes exhibited only the averaged olefinic proton resonances at down to −60 °C.[5,6] We assume that much lower lability of the palladium–olefin bond in the complex of type **4** is a consequence of the fulfillment of the

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(4) (a) Pestrikov, S. V.; Moiseev, I. I.; Tsvilikhovskaya, B. A. *Russ. J. Inorg. Chem.* **1966**, *11*, 930. (b) Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1595.

(5) Ban, E.; Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1974**, *69*, 455.

(6) Partenheimer, W.; Durham, B. *J. Am. Chem. Soc.* **1974**, *96*, 3800.

(7) Majima, T.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *134*, C45.

(8) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. (b) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426 and references therein. (c) Lennon, P.; Madhavarao, M.; Rosan, A. M.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (d) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305 and references therein. (e) Powell, P. *J. Organomet. Chem.* **1979**, *165*, C43.

(9) Kurosawa, H.; Asada, N. *Tetrahedron Lett.* **1979**; 255.

(10) Majima, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1977**, 610.

(11) (a) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596. (b) Uson, R.; Fornies, J.; Martinez, F. *J. Organomet. Chem.* **1976**, *112*, 105.

(12) Cross, R. J.; Wardle, R. *J. Chem. Soc. A* **1971**, 2000.

(13) Compare, for example, $\Delta\delta$ ($\delta_{free} - \delta_{complex}$) for C_2H_4 (1.22 ppm) or *cis*-MeC*H*═C*H*Me (0.73) of $[Pd(C_5H_5)(PBu_3)(olefin)]^+$ with those (−0.12, −0.88) of $[PdCl_2(olefin)]_2$.[14] Furthermore, $\Delta\delta$ in Table III are also much greater than those (3–10 ppm) of $PdCl_2(diolefin)$[15] and rather comparable to those of $PtCl_2(py)(olefin)$[16] and $[PtCl_3(olefin)]^-$.[17]

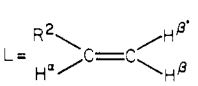
(14) Partenheimer, W. *J. Am. Chem. Soc.* **1976**, *98*, 2779.

(15) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

(16) Meester, M. A. M.; van Dam, H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1976**, *20*, 155.

(17) Cooper, D. G.; Powell, J. *Inorg. Chem.* **1976**, *15*, 1959.

Table II. ^{1}H NMR Data^a of $[Pd(C_5H_5)(PR^1{}_3)(L)]ClO_4$



compd			δ			
no.	R^1	R^2	H^α	$H^{\beta'}$	H^β	C_5H_5
4a	C_6H_5	H	4.03 (J_P = 2.5)			5.98 (J_P = 2.5)
4b	C_6H_5	CH_3^{b}	*c*	3.23 (J_{H^α} = 7)	*c*	5.93 (J_P = 2.5)
4d	C_6H_5	C_6H_5	5.26 (J_P = 3.0, $J_{H\beta}$ = 8.3, $J_{H\beta'}$ = 15.8)	3.24 (J_P = 2.6)	5.56	5.49 (J_P = 2.6)
4g^d	C_2H_5	C_6H_5	6.03 (J_P = 2.4, $J_{H\beta}$ = 8.3, $J_{H\beta'}$ = 15.8)	3.72 (J_P = 1.9)	5.19	5.68 (J_P = 2.4)
4k^d	*n*-C_4H_9	C_6H_5	6.01 (J_P = 2.6, $J_{H\beta}$ = 8.4, $J_{H\beta'}$ = 15.0)	3.70 (J_P = 1.8)	5.13	5.64 (J_P = 2.6)
4q	*n*-C_4H_9	H	4.14 (J_P = 1.8)			6.03 (J_P = 2.3)
4r	C_6H_5	*p*-$NO_2C_6H_4$	*e*	3.47 (J_{H^α} = 8.3)	*e*	5.62 (J_P = 2.5)
4s	C_6H_5	*p*-$NMe_2C_6H_4$	*e*	2.80 (J_{H^α} = 8)	*e*	5.55 (J_P = 2.4)
4t	*n*-C_4H_9	*p*-$NMe_2C_6H_4$	6.18 ($J_{H\beta}$ = 8.3, $J_{H\beta'}$ = 15.0)	3.38	4.95	5.66^f

^{a} In $CDCl_3$ unless otherwise noted. *J* values in hertz. ^{b} δ_{CH_3} 1.97 (J_{H^α} = 5.3 Hz). ^{c} Broad multiplets centered at δ 4.69. ^{d} *J* values in acetone. ^{e} Obscured by other resonances. ^{f} J_P not determined.

Table III. ^{13}C NMR Data^a of $[M(C_5H_5)(PR^1{}_3)(L)]ClO_4$ ($L = R^2HC^\alpha{=}C^\beta H_2$)

compd				δ					
no.	M	R^1	R^2	C^α	(Δδ)	C^β	(Δδ)	C_5H_5	(J_P, Hz)
4h	Pd	*n*-C_4H_9	*p*-$NO_2C_6H_4$	87.8	(47.1)	58.8	(59.9)	103.9	(1.2)
4j			*p*-ClC_6H_4	91.0	(44.7)	56.6	(57.8)	103.6	(1.2)
4k			C_6H_5	92.1	(44.8)	56.2	(56.9)	103.3	(1.8)
4l			*p*-$CH_3C_6H_4$	93.2	(43.6)	55.6	(57.1)	103.4	(1.9)
4m			*p*-$CH_3OC_6H_4$	94.5	(41.8)	54.4	(57.1)	103.3	(1.8)
4q			H	65.7	(56.8)			101.5	(1.8)
6	Pt	C_6H_5	H	42.6^b	(79.9)			97.8^c	(1.8)

^{a} In $CDCl_3$. ^{b} J_{Pt} = 223.4 Hz. ^{c} J_{Pt} = 16.2 Hz.

Table IV. Relative Stability of Cationic Palladium(II) Complexes^a

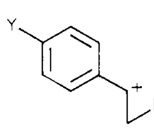
	R = C_6H_5		R = *n*-C_4H_9
L	X = ClO_4	X = BF_4	X = ClO_4
CO	(1.7 ± 0.2) × 10^3		
$C_6H_5SCH_3$	(2.0 ± 0.2) × 10^2		
C_6H_5CN	1.41 ± 0.10		
$CH_2{=}CH_2$	13.5 ± 0.6		
$CH_2{=}CHCH_3$	1.14 ± 0.09		
cis-$CH_3CH{=}CHCH_3$	0.22 ± 0.05		
trans-$CH_3CH{=}CHCH_3$	0.04 ± 0.01		
$CH_2{=}C(CH_3)_2$	<10^{-2}		
$CH_2{=}CHC_6H_4Y$			
Y = *p*-NO_2	0.051 ± 0.005	0.050 ± 0.005	0.13 ± 0.02
m-NO_2		0.051 ± 0.005	
p-COMe			0.29 ± 0.03
p-Cl	0.29 ± 0.03	0.35 ± 0.04	0.50 ± 0.07
m-Cl		0.16 ± 0.02	
H	0.63 ± 0.06^b	0.62 ± 0.06	0.88 ± 0.09
p-Me	1.02 ± 0.10	1.05 ± 0.11	1.33 ± 0.20
m-Me		0.85 ± 0.09	
p-OMe	1.95 ± 0.29	1.62 ± 0.24	1.52 ± 0.22
p-NMe_2	8.5 ± 2.0	8.9 ± 2.1	4.2 ± 0.8

^{a} Expressed by *K* of the following equilibrium in $CDCl_3$ at 23 °C except for substituted styrene series with $PR_3 = PPh_3$ at −2 °C. $[Pd(C_5H_5)(PR_3)(CH_3C_6H_4CN\text{-}o)]X + L \rightleftarrows [Pd(C_5H_5)(PR_3)\cdot(L)]X + CH_3C_6H_4CN\text{-}o$ (*K*). ^{b} At 23 °C, 0.36 ± 0.05.

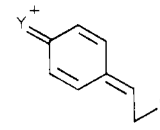
18-electron configuration around palladium. Clearly a bimolecular pathway for ligand exchange, a process common in 16-electron palladium(II) complexes, must be unfavorable in the 18-electron complexes.[18] A greatly different lability of the metal–olefin bond between 16- and 18-electron complexes was also noted in $Rh(acac)(C_2H_4)_2$ and $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$.[20]

There appears to be an empirical trend[21] that those complexes which bear more electron density on the metal exhibit larger coordination shifts of olefinic carbon resonances.[22] Roughly parallel trends of ^{1}H shifts to those of ^{13}C shifts were also noted.[21,23] Thus, the observation 3 above may have been caused by the electron-donating nature of the Cp ligand (compare the ν(CO) (2113 cm^{-1}) of **5** with those (2135, 2143 cm^{-1})[11] of $[PdCl(PEt_3)_2(CO)]^+$ and $[Pd(C_6F_5)(PPh_3)_2(CO)]^+$).

It seems also appropriate to refer to the variation of ^{13}C shifts in a series of substituted styrene complexes (Table III). The Δδ for C^α are larger in complexes of the more electron-withdrawing styrenes,[24] and linear regression analysis showed a better correlation between $\Delta\delta_{C^\alpha}$ and the Hammett σ^+ values (slope = 3.35 ppm, *r* = 0.997) than the σ values (slope = 4.32 ppm, *r* = 0.934), as was the case[17] for substituted styrene complexes of platinum(II). From such correlation in the latter system Powell and co-workers indicated the increased ionic contribution, A and B, to the platinum–styrene bonding with the increased π-donor ability of Y. However, to how much extent such canonical forms make contribution to the overall thermodynamics of the complexes may be very difficult to estimate solely from the ^{13}C NMR data (see the later discussion concerning a different substituent dependency of ^{13}C NMR and stability data).



A



B

Configuration of Olefin–Palladium(II) Complex. In square-planar olefin–platinum(II) complexes such as **8**, the C=C bond

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[18] Even certain Pt^{II} complexes with the 16-electron configuration are known to contain the very labile Pt–olefin bond.[19]

[19] (a) Cramer, R. *Inorg. Chem.* **1965**, *4*, 445. (b) Kaplan, P. D.; Schmidt, P.; Orchin, M. *J. Am. Chem. Soc.* **1967**, *89*, 4537.

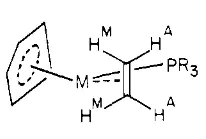
[20] Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.

[21] (a) Tolman, C. A.; English, A. D.; Manzer, L. E. *Inorg. Chem.* **1975**, *14*, 2353. (b) Yamamoto, T.; Ishizu, J.; Komiya, S.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *171*, 103.

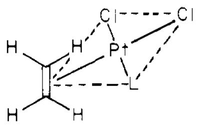
[22] For further discussions of ^{13}C NMR data, see: Evans, J.; Norton, J. R. *Inorg. Chem.* **1974**, *13*, 3042.

[23] Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 135.

[24] Among Δδ for the three olefin proton resonances in **4h** and **4j–m**, those of H^α [0.60 (MeO) < 0.65 (Me) < 0.68 (Cl) < 0.72 (H) < 0.9 (NO_2)] showed a similar but much narrower range of variation.



4a, M = Pd, R = Ph
4q, M = Pd, R = Bu
6, M = Pt, R = Ph

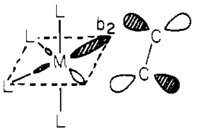


8

of the coordinated olefin is oriented perpendicular to the coordination plane at its equilibrium position but rotates with considerable ease about the metal–olefin axis.[25] Both configuration and rotation of the olefinic ligand have received considerable attention also in complexes of the type $Rh(\eta^5\text{-}C_5R_5)(L)(C_2H_4)$ (R = H, Me; L = C_2H_4, C_2F_4, PPh_3)[20,26,27] in the context of the nature of the olefin–metal bonding. Little is known, however, about the rotation of olefins in palladium(II) complexes.

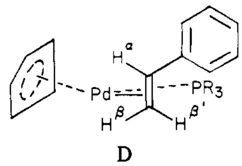
It may reasonably be assumed that the ethylene molecule in the ground state of **4a** and **4q** also is located perpendicular to the coordination plane, as in their isoelectronic counterpart $Rh(\eta^5\text{-}C_5Me_5)(PPh_3)(C_2H_4)$[27] (see also the later discussion). The ^1H NMR spectra of **4a** and **4q** in $CDCl_3$ showed one sharp doublet at room temperature (Table II) and only a little broader singlet (half-height width ca. 7 Hz) at −80 °C in CD_2Cl_2 or acetone for the ethylene protons, indicating rapid rotation of ethylene about the Pd–olefin axis. In the platinum analogue **6**, the variable-temperature ^1H NMR spectral features are quite reminiscent of those of **8**.[25] Thus, a somewhat broad singlet in CD_2Cl_2 at 23 °C [δ 2.97 (J_{Pt} = 70 Hz)] for the ethylene protons of **6** was converted[28] to AA′MM′X (X = ^{31}P) multiplets at −60 °C [δ_A 2.02, δ_M 3.75 ($J_{AA'} = J_{MM'} = 6$, $J_{AM'} = 13$, $J_{AX} = 4.4$, $J_{APt} = 64$, $J_{MPt} = 76$ Hz)].[29]

In view of the similar covalent radii of Pd^{II} and Pt^{II},[31] steric hindrance with regard to ethylene rotation in **6** is assumed to be not too much different from that in **4a**. We propose that an apparently large difference of the rotational barrier between **6** and **4a** is attributed primarily to a difference in the energy level of the ground-state configuration. The ground state of **6** may be lowered relative to that of **4a** as a consequence of more effective π back-bonding from platinum to ethylene than from palladium; compare also ν(CO) of **5** (2113 cm^{-1}) with that of **7** (2081 cm^{-1}). Such π interaction in **6** is thought to be similar in nature to that between the metal b_2 and ethylene π^* orbitals (C) in d^8 ML_4-($CH_2{=}CH_2$) complexes, the latter being shown by a frontier MO analysis to play an important role in stabilizing the ground state of the $ML_4(CH_2{=}CH_2)$.[32] It is to be noted here that a small distortion of the ML_4 fragment and substitution of the Cp group for three L's cis to each other would lead to a rough representation of the $M(\eta^5\text{-}C_5H_5)L$ fragment.

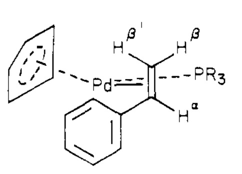


C

For the styrene–palladium complexes, occurrence of rotational isomerism (typically D and E without regard to optical isomers) is possible. The X-ray crystal study[33] revealed the structure of $[Pd(\eta^5\text{-}C_5H_5)(PEt_3)(styrene)]BF_4$ to be close to D with a slight rotation of the C═C bond about the palladium–olefin axis in such a way as to take the phenyl group away from the phosphine group (a twist angle ca. 13°). The observed Pd–C^α (2.23 Å), Pd–C^β (2.18 Å), and C^α–C^β (1.38 Å) lengths are normal. On the other hand, examination of the ^1H NMR spectra of **4d**, **4g**, and **4k** suggests, though not conclusively, that a dominant rotamer in solutions is E. The shape of the absorptions in the spectra of **4d** and **4k** in $CDCl_3$ showed almost no temperature dependence at down to −50 °C, and the olefinic proton peaks of **4k** in acetone became somewhat broad at −80 °C. More detail of low-temperature spectra could not be given due to limited solubilities. As shown in Table II, as the PR_3 varies from PEt_3 or PBu_3 to PPh_3, the chemical shift of $H^{\beta'}$ moves in the direction opposite to those of H^α and H^β. The change of the shift of $H^{\beta'}$ is in line with the change of the basicity of the phosphines, but the higher field movement of H^α and H^β in **4d** is most probably associated with a diamagnetic shielding effect of the P-phenyl rings. Furthermore, the H^α and H^β resonances in all of **4d**, **4g**, and **4k** exhibited observable spin couplings with ^{31}P, while such couplings could not be resolved well for the H^β resonances. By comparing these spectral features with those of **6** observed at −60 °C, it is probable that E or a conformation close to E makes a dominant contribution to the observed spectra of the styrene complexes.



D



E

Relative Stability of Olefin–Palladium Complex. By virtue of the ^1H NMR characteristics described before, the relative concentrations of the equilibrium species in eq 2 could readily be determined by integration of appropriate signals. The use of benzonitrile or *o*-tolunitrile complexes as one component in equilibria was of particular help to the comparison of the stabilities of a wide variety of olefin complexes owing to simplicity of the spectra[34] and ease of preparation in the case of the PPh_3 derivatives. A similarly simple spectral pattern of the thioanisole complex[34] was also convenient for the purpose of comparing the stabilities of the carbonyl (**5**) and the ethylene (**4a**) complexes. In Table IV are shown relative stability constants of the substituted ethylene and styrene complexes as well as other related complexes including the carbonyl.

Carbon monoxide is seen as by far a stronger ligand to palladium(II) in $Pd(\eta^5\text{-}C_5H_5)(PR_3)$ moiety compared to olefins. In particular, the relative stability of the carbonyl and the ethylene complex, $K(CO)/K(C_2H_4) = 1.3 \times 10^2$ in the present system, is larger than the corresponding value (30)[35] for the equilibrium $Cu^+ + L \rightleftharpoons CuL^+$ (H_2O). Apparently the severer steric requirement for complexation in the former system would contribute, in part, to a greater degree of discrimination between the ligating ability of these two compounds in the former. The trend in the relative stability order in a series of methyl-substituted ethylene complexes (Table IV) is similar to those of the corresponding series of other complex systems where the steric interaction between the methyl and the ancillary ligands is the main cause for the stability order.[5] The intramolecular steric congestion in the present complex system is such that cyclohexene showed almost no indication of complex formation.

Rather scattered stability trends were previously observed in a series of substituted styrene complexes of different metals such as Pd^{II},[5] Pt^{II},[36] and Ag^I.[37] Yet the most puzzling was a marked

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[25] Ashley-Smith, J.; Douek, I.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1776 and references therein.

[26] Guggenberger, L. J.; Cramer, R. *J. Am. Chem. Soc* **1972**, *94*, 3779.

[27] Porzio, W.; Zocchi, M. *J. Am. Chem. Soc.* **1978**, *100*, 2048.

[28] The energy barrier to the rotation in 6 at the coalescence temperature (0 °C) was estimated as ca. 13.0 kcal/mol by the method shown in ref 25.

[29] We assign the protons A as those close to PPh_3 and M close to Cp on the basis of the difference in J_{Pt} (see ref 25). This is in further agreement with the large diamagnetic shielding effect of the P-Ph rings on the protons in the ligands cis to PPh_3.[30]

[30] Kurosawa, H. *Inorg. Chem.* **1975**, *14*, 2148.

[31] X-ray crystal studies indicate that various Pd-ligand bond distances are similar to the corresponding Pt-ligand distances in two metal complexes sharing the same or similar compositions: Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science: London, 1973.

[32] Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

[33] Miki, K.; Kasai, N., private communication.

[34] The δ values ($CDCl_3$) of Me of *o*-tolunitrile or thioanisole are 2.52 (free) and 2.07 (complex containing PPh_3) or 2.48 (free) and 2.74 (complex).

[35] Ogura, T. *Inorg. Chem.* **1976**, *15*, 2301.

[36] (a) Shupack, S. I.; Orchin, M. *J. Am. Chem. Soc.* **1964**, *86*, 586. (b) Joy, J. R.; Orchin, M. *Ibid.* **1959**, *81*, 305.

Table V. Hammett Equations[a] for Stability of Substituted Styrene Complexes, $[Pd(C_5H_5)(PR_3)(styrene)]X$

compd					
R	X	$-\rho$	(r)	$-\rho^+$	(r)
C_6H_5	ClO_4	1.40	(0.997)	0.84	(0.974)
C_6H_5	BF_4[b]	1.39	(0.999)	0.83	(0.974)
C_6H_5	BF_4[c]	1.44	(0.998)	0.88	(0.964)
n-C_4H_9	ClO_4	0.94	(0.996)	0.56	(0.956)

[a] By linear regression analysis using K values shown in Table IV. [b] Para substituents only. [c] Para and meta substituents.

Table VI. Thermodynamic Data for the Equilibrium Shown in Table IV ($R = C_6H_5$, $L = CH_2{=}CHC_6H_4Y$-p)

X	Y	$-\Delta G°$ (271 K) kcal/mol	$-\Delta H°$ kcal/mol	$-\Delta S°$ (271 K) cal/(mol deg)
ClO_4	NO_2	−1.6 ± 0.1	0.6 ± 0.5	8.1 ± 2.1
	Cl	−0.7 ± 0.1	2.0 ± 0.3	9.9 ± 1.1
	H	−0.3 ± 0.1	3.2 ± 0.3	12.8 ± 1.1
	Me	0.0 ± 0.1	3.8 ± 0.5	14.1 ± 1.8
	OMe	0.4 ± 0.1	3.7 ± 0.4	12.2 ± 1.7
	NMe_2	1.2 ± 0.1	6.0 ± 1.4	17.9 ± 5.8
BF_4	NO_2	−1.6 ± 0.1	4.2 ± 0.3	21.3 ± 1.3
	Cl	-0.6 ± 0.1	5.3 ± 0.7	21.5 ± 2.6
	H	−0.3 ± 0.1	5.1 ± 0.5	19.9 ± 2.0
	Me	0.0 ± 0.1	5.5 ± 0.7	20.3 ± 2.6
	OMe	0.3 ± 0.1	5.8 ± 0.6	20.4 ± 2.5
	NMe_2	1.2 ± 0.2	6.6 ± 1.6	20.1 ± 6.3

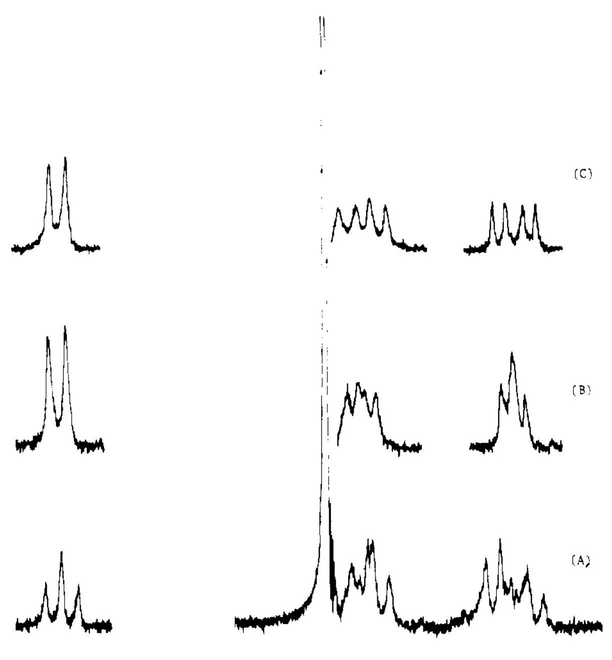

Figure 1. ^1H NMR spectra of **9** prepared from **4a**-C_2H_4 (A), **4a**-*cis*-CHD=CHD (B), and **4a**-*trans*-CHD=CHD (C).

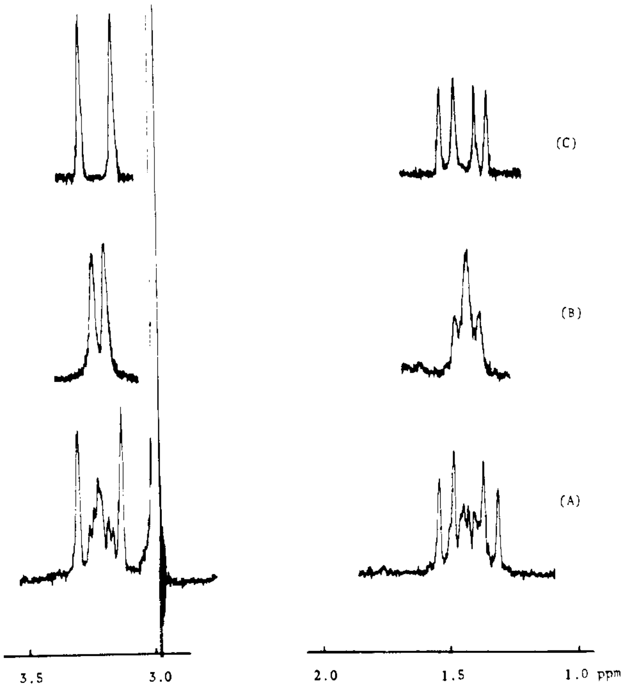

Figure 2. ^1H NMR spectra of **10a** prepared from **4a**-C_2H_4 (A), **4a**-*cis*-CHD=CHD (B), and **4a**-*trans*-CHD=CHD (C).

difference in the type of dependency of the stabilities and ^{13}C NMR data of platinum(II) complexes upon the electronic nature of the substituents; there was a good linear relationship between the ^{13}C NMR data and the Hammett σ^+,[17] while no such linear correlation existed between the stabilities and any Hammett parameters.[36] In the present palladium complexes where ^{13}C NMR data are also correlated with σ^+ (see before), plots of log K in Table IV for the styrene series against σ, rather than σ^+, gave the better lines, as summarized in Table V. The result involving the meta substituents suggests that the steric factor of these substituents exerts only a minor influence on the center of the metal–olefin interaction. The negative sign of ρ is in line with the dominant σ interaction in the Pd–styrene bond. On the other hand, the more effective π interaction in the Pt–styrene bond is presumably responsible for the more complex pattern of the substituent dependency of the stability in the platinum complexes.

The type of correlation observed as in Table V is somehow surprising, since in a series of styrene complexes of type **2**, a linear free-energy relationship was found to hold when the σ^+ parameters are employed.[5] From the latter result, occurrence of an important contribution of the ionic resonance forms A and B to the stability of the palladium–styrene bond was indicated. It is then not unreasonable to expect that such canonical forms are more significant in the cationic complexes. It is possible that occurrence of ionic association of **4** in solutions affects the type of Hammett equation. Electric conductance measurements of **4j**, **4k**, and **4m–p** in CH_2Cl_2 at 25 °C indicated that the hypothetical 1:1 ion-pair formation constant, calculated by the Fuoss method,[38] lies in the order of more than 10^3 (see Experimental Section). Clearly under NMR experimental conditions ($\geq 5 \times 10^{-2}$ M), the complexes are expected to exist predominantly as 1:1 ion pairs or higher aggregates, though their precise structures are not known. If the notion[39] that the degree of orientation of solvent molecules is greater around free ions than in the vicinity of ion pairs is allowed to apply in the present complexes, the contribution of A and B, which was suggested to exhibit an increased solvation requirement with increasing π-donor ability of the substituent,[5] would become less important in the ionic aggregates. It is noteworthy in this context that $\Delta S°$ values in the present complexes (Table VI) are either almost constant or less substituent sensitive than those in **2**.[5]

Reaction with 2,4-Pentanedionate and Alkoxy Anions. Olefins coordinated with certain metals are known to be susceptible to nucleophilic attack.[8] This process involving palladium is one of the most fundamental steps in understanding the mechanism of some synthetic reactions.[2,40] However, intermediate alkylpalladium(II) complexes have not been isolated except in reactions

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(37) Fueno, T.; Okuyama, T.; Deguchi, T.; Furukawa, J. *J. Am. Chem. Soc.* **1965**, *87*, 170.

(38) Fuoss, R. M. *J. Am. Chem. Soc.* **1935**, *57*, 488.

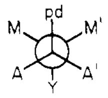
(39) Szwarc, M. *Acc. Chem. Res.* **1969**, *2*, 87.

(40) (a) Murahashi, S.; Yamamura, M.; Mita, N. *J. Org. Chem.* **1977**, *42*, 2870. (b) Holton, R. A.; Kjonaas, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 4177. (c) Hayashi, T.; Hegedus, L. S. *Ibid.* **1977**, *99*, 7093. (d) James, D. E.; Hines, L. F.; Stille, J. K. *Ibid.* **1976**, *98*, 1806. (e) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *Ibid.* **1979**, *101*, 2411.

involving olefin substrates capable of chelate coordination.[3,40b] Now the ethylene complex **4a** has been found to react with sodium 2,4-pentanedionate and alkoxides to afford good yields of stable alkyl complexes, **9** and **10**, respectively (eq 3). In contrast to

$$\begin{gathered} \mathbf{4a} \xrightarrow{NaY} Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2CH_2Y) \qquad (3) \\ \mathbf{9},\ Y = CH(COMe)_2 \\ \mathbf{10a},\ Y = OMe \\ \mathbf{10b},\ Y = O\text{-}i\text{-}Pr \end{gathered}$$

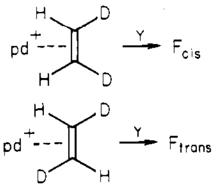
the failure to deduce any conformational information from the ^1H NMR spectra of the organoiron(II) analogues $FpCH_2CH_2Y$ [$Fp = Fe(\eta^5\text{-}C_5H_5)(CO)_2$; $Y = CH(COOMe)_2$, OMe],[8b,c] the ethylene group proton resonances of **10** appeared as AA'MM' multiplets, from which as well as the spectra of **9** and **10** prepared from the *cis*- or *trans*-ethylene-d_2 complex (Figures 1 and 2) the following conformation (F) was indicated to dominate in solutions.



F, A = A' = M = M' = H

F_{cis}, A = M = H, A' = M' = D

F_{trans}, A = M' = H, A' = M = D



pd = Pd(η^5-C_5H_5)(PPh_3)

The spectra of the deuterium analogues of **9** and **10** are of particular help in deducing the trans addition of palladium and Y^- to ethylene. Such stereospecifically labeled alkylpalladium(II) compounds are well suited for stereochemical studies of Pd–C bond cleavage, details of which will be given elsewhere.

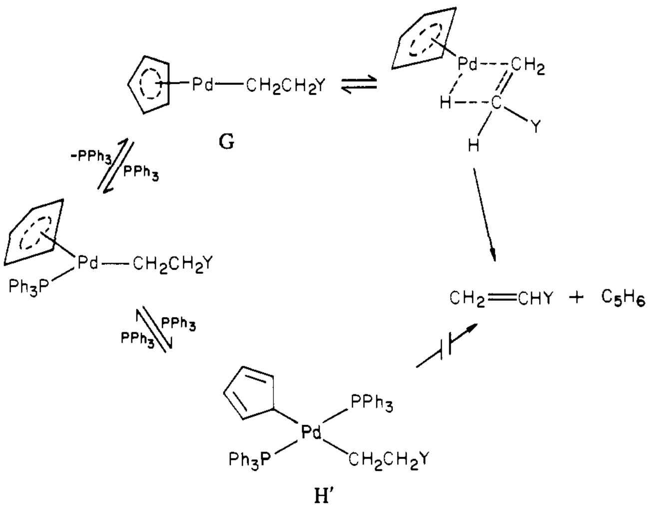
Reactions of **4a** with diethylamine or pyridine at −50 °C gave no alkylpalladium(II) complexes but gave the amine–palladium(II) complexes plus ethylene; some olefin–platinum(II) complexes are known to react readily with amines to give β-aminoalkylplatinum(II) complexes.[41] Treatment of the styrene complex **4d** with the methoxy anion gave no characterizable products, while a low yield of $Pd(\eta^5\text{-}C_5H_5)(PPh_3)[CH(COMe)_2]$ (**11**) was confirmed to be present among several products from **4d** and $NaCH(COMe)_2$. **11** was also obtained by the reaction of $TlCH(COMe)_2$ with $Pd(\eta^5\text{-}C_5H_5)(PPh_3)(Br)$. Interestingly, **11** failed to undergo any reaction with ethylene when a stream of ethylene gas was passed through a solution of **11**. However, this observation as well as the stereochemical result shown above may not necessarily be taken as evidence to exclude a possibility of cis attack of the β-diketo and the methoxy anions at olefins in palladium complexes bearing other coordination environments. The reason for this is that the concurrent coordination of ethylene and the nucleophile to palladium, a requisite for the cis insertion, is thought an unfavorable process in the present case due to the relatively low lability of the ligands in the $Pd(\eta^5\text{-}C_5H_5)(PPh_3)$ moiety; a 20-electron intermediate would be formed if these ligands remain coordinated during the cis insertion.

Complexes **9** and **10** decomposed in benzene at elevated temperatures (≥50 °C) via β-hydrogen elimination and subsequent collapse of the Pd-H intermediate to give cyclopentadiene and olefins, as in the decomposition of $Pd(\eta^5\text{-}C_5H_5)(PPh_3)(n\text{-}C_4H_9)$ (eq 4).[42] The observations described below strongly suggest that

$$Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2CH_2Y) \rightarrow CH_2{=}CHY + C_5H_6 \qquad (4)$$

the β-elimination occurs from an intermediate, $Pd(\eta^5\text{-}C_5H_5)(CH_2CH_2Y)$ (**G**), formed by dissociation of PPh_3. This is understandable in view of the 18-electron configuration in **9** and **10** and the increase in the coordination number during the β-elimination. We believe that the low lability of the ancillary ligands in these complexes is again responsible for successful isolation of the otherwise unstable substituted ethylpalladium(II) compounds.

Scheme I



Reaction 4 was found to be retarded by addition of free PPh_3 but accelerated dramatically by an equimolar quantity of *m*-chloroperbenzoic acid (MCPBA) (see Experimental Section). Furthermore, this reaction took place more rapidly under aerobic condition than in vacuo. Most of the PPh_3 of the starting material was converted to $O{=}PPh_3$ after the thermolysis with MCPBA or in air. Since no change was observed in the ^1H NMR spectra of **9** and **10** in the presence of free PPh_3 (P/Pd = 1), it is deduced that there is no accumulation of any spectroscopically detectable amounts of an adduct between PPh_3 and **9** or **10**. Likewise, no accumulation of a PPh_3-dissociated product in the solution of **9** or **10** is suggested. We then assume that the β-elimination occurs after PPh_3 dissociates rather slowly,[43] as in the analogous decomposition of $Fe(\eta^5\text{-}C_5H_5)(PPh_3)(CO)(n\text{-}C_4H_9)$.[44] It is highly possible that thermolysis under air, dioxygen, and a zerovalent Pd complex containing PPh_3, which would have been formed initially, is able to effectively trap even a very small quantity of PPh_3 freed from **9** or **10**. A catalytic oxidation of PPh_3 to $O{=}PPh_3$ using $Pd(PPh_3)_2(O_2)$ was reported.[45] MCPBA is by far the better oxidant toward PPh_3.

Having discussed the role of PPh_3 dissociation in the β-elimination, we further point out a different effect of the phosphine on the reaction course. Although excess PPh_3 had no actual effect on the NMR spectra of **9** or **10**, we suggest occurrence of intermolecular exchange of PPh_3 with its rate much slower than the NMR time scale through an *associative* mechanism on the basis of the following. Thus, we observed the facile phosphine exchange (eq 5) at 23 °C, whose kinetics obey a first-order dependence of the concentrations of both **10a** and PR_3, as determined by ^1H NMR in benzene [$k_5 = (6.9 \pm 0.7) \times 10^{-2}$, $k_{-5} = (1.8 \pm 0.2) \times 10^{-2}$ L/(mol s)].

$$\begin{gathered} Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2CH_2OMe) + P(C_6H_4OMe\text{-}p)_3 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \\ Pd(\eta^5\text{-}C_5H_5)[P(C_6H_4OMe\text{-}p)_3](CH_2CH_2OMe) + PPh_3 \qquad (5) \end{gathered}$$

The most plausible intermediate in this exchange would then be a η^1-Cp complex, $Pd(\eta^1\text{-}C_5H_5)(PPh_3)[P(C_6H_4OMe\text{-}p)_3](CH_2CH_2OMe)$ (**H**). Formation of $Pd(\eta^1\text{-}C_5H_5)(PR_3)(PR'_3)(Br)$ (R = R' = Et; R = Et, R' = Ph) from

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[41] (a) Kaplan, P. D.; Schmidt, P.; Orchin, M. *J. Am. Chem. Soc.* **1968**, *90*, 4175. (b) de Renzi, A.; di Blasio, B.; Panunzi, A.; Pedone, C.; Vitagliano, A. *J. Chem. Soc., Dalton Trans.* **1978**, 1392 and references therein.

[42] Felkin, H.; Turner, G. K. *J. Organomet. Chem.* **1975**, *129*, 429.

[43] Kinetic examination of thermolysis in the presence of added PPh_3 was difficult owing to an increasing degree of unidentified decomposition pathway(s) with increasing PPh_3.

[44] Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789.

[45] Wilke, G.; Schott, H.; Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 92.

$Pd(\eta^5\text{-}C_5H_5)(PEt_3)(Br)$ and PR'_3 has been confirmed spectroscopically.[12] These results then lead to an interesting contrast between the ability of two coordinatively unsaturated intermediates, G and H′ (see Scheme I), to undergo the β-hydrogen elimination. The reason for such different behavior of G and H′ may partly be of steric origin; in the transition state from G to the β-elimination there would be more room for the developing C═C bond and the hydrido ligand to coordinate to palladium than in that from H′. In this regard it may be noted that the β-elimination of another 16-electron complex, $Pt(PPh_3)_2(n\text{-}C_4H_9)_2$, required further reduction of the coordination number via dissociation of PPh_3.[46,47] Similarly, kinetic evidence was presented to suggest the need of a vacant site for the β-elimination of 16-electron, 4-coordinate alkylpalladium(II) intermediates during the Pd-catalyzed oxidation of olefins.[48]

Experimental Section

Caution! Care must be taken in handling all the potentially explosive compounds containing the perchlorate anion.

Preparation of 4. All of the compounds shown in Table I were prepared by essentially the same method involving addition of an acetone solution of AgX (X = ClO_4, BF_4) to an equimolar quantity of $Pd(\eta^5\text{-}C_5H_5)(PR_3)(Br)$ (R = Ph, Et, Bu)[12] in CH_2Cl_2 containing a large excess of olefinic ligands with the solution kept at less than 0 °C. After AgBr was filtered off, hexane (for R = Ph) or hexane plus ethanol (for R = Et, Bu) was added to the filtrate at 0 °C to cause crystallization of complexes. Yields were generally good (≥60%).

Preparation of Other Cationic Palladium Complexes. A procedure to obtain the following complexes was essentially the same as that described above. $[Pd(C_5H_5)(PPh_3)(CO)]ClO_4$: violet powders; mp 167 °C dec; anal. ($C_{24}H_{20}O_5PClPd$) C, H; ^1H NMR ($CDCl_3$) δ 5.99 (d, J_P = 2.3 Hz, Cp); IR (CH_2Cl_2) 2113 cm^{-1} (CO). $[Pd(C_5H_5)(PPh_3)(C_6H_5CN)]ClO_4$: blue microcrystals; mp 135 °C dec; anal. ($C_{30}H_{25}NO_4PClPd$) C, H, N; ^1H NMR ($CDCl_3$) δ 5.88 (d, J_P = 2.3 Hz, Cp); IR (Nujol) 2270 cm^{-1} (CN). $[Pd(C_5H_5)(PPh_3)(CH_3C_6H_4CN)]ClO_4$: blue crystals; mp 145–146 °C dec; anal. ($C_{31}H_{27}NO_4PClPd$) C, H, N; ^1H NMR ($CDCl_3$) δ 5.84 (d, J_P = 2.3 Hz, Cp), 2.07 (s, Me); IR (Nujol) 2270 cm^{-1} (CN). $[Pd(C_5H_5)(PPh_3)(CH_3C_6H_4CN)]BF_4$: blue microcrystals; mp 138–140 °C dec; anal. ($C_{31}H_{27}NBF_4PPd$) C, H, N. $[Pd(C_5H_5)(PPh_3)(C_6H_5SCH_3)]ClO_4$: blue-violet crystals; mp 157–158 °C dec; anal. ($C_{30}H_{28}O_4PSClPd$) C, H; ^1H NMR ($CDCl_3$) δ 5.80 (d, J_P = 2.3 Hz, Cp), 2.74 (s, Me).

Preparation of 6 and 7. Cyclopentadienylthallium (54 mg; 0.2 mmol) was added to a CH_2Cl_2 solution (10 mL) of $PtCl_2(PPh_3)(C_2H_4)$ (0.2 mmol) at 0 °C. After 30 min, $AgClO_4$ (0.2 mmol) in acetone (2 mL) was added. The mixture was filtered, and the filtrate was dried under vacuum. The resulting solids were recrystallized from CH_2Cl_2–diethyl ether to give orange crystalline products of $[Pt(C_5H_5)(PPh_3)(C_2H_4)]ClO_4$ (13%), mp 170 °C dec: anal. ($C_{25}H_{24}O_4PClPt$) C, H; ^1H NMR ($CDCl_3$) δ 5.95 (d, J_P = 2.0 Hz, J_{Pt} = 14.5 Hz, Cp), 2.97 (br s, J_{Pt} = 70.0 Hz, C_2H_4). In a similar way, 74% of orange crystalline $[Pt(C_5H_5)(PPh_3)(CO)]ClO_4$, mp 195 °C dec, was obtained: anal. ($C_{24}H_{20}O_5PClPt$) C, H; ^1H NMR ($CDCl_3$) δ 5.96 (d, J_P = 2.2 Hz, J_{Pt} = 14.3 Hz, Cp); IR (CH_2Cl_2) 2081 cm^{-1} (CO).

Relative Stability. The equilibrium constants of eq 2 were measured by the ^1H NMR method with NMR tubes kept in a constant temperature probe (±1 °C). The thermodynamic parameters for a series of substituted styrene complexes containing PPh_3 (Table VI) were obtained from plots of $1/T$ vs. log K at 10, 5, −2, and −9 °C. The concentrations of the palladium(II) complexes ranged from ca. 5×10^{-2} to 5×10^{-1} M, and the K values shown in Table IV are averages of the results with at least three samples containing different reagent ratios and concentrations. An equilibrium mixture containing the benzonitrile complex as one component and the ethylene, substituted ethylene, or *o*-tolunitrile complex as the other was prepared by weighing into a tube the benzonitrile complex and methyl β-naphthyl ether as an internal reference, to which was added $CDCl_3$ containing the free ligand. The ligand signals (free and coordinated) were integrated against the methoxy signal (δ 3.89) of the reference. All the styrene complexes except for **4t** were equilibrated with the *o*-tolunitrile complex starting from a styrene complex and free *o*-tolunitrile and/or vice versa. **4t** was formed by adding a known amount of (*N*,*N*-dimethylamino)styrene to the solution of a known amount of **4k**, with the relative concentration being measured by integrating the H^β signals (see Table II). By saturating a $CDCl_3$ solution of the thioanisole complex with carbon monoxide gas (CO concentration, 8×10^{-3} M),[49] we equilibrated this complex with **5**, and the Cp as well as SMe signals were integrated. **4a** and the thioanisole complex were examined similarly.

Electric Conductance. Electric conductance measurements were carried out in CH_2Cl_2 at 25 °C by using a TOA conductmeter, Model CM-15A, and a TOA conductivity cell, CG-7001PL. In order to avoid decomposition of the complexes during measurements, we added an ca. 10-fold excess of the free styrenes to the complex solutions of 5×10^{-4}–10^{-5} M concentrations. The 1:1 ion-pair formation constant and Λ_0 calculated by the Fuoss method[38] are as follows: 7.6×10^3 L/equiv, 92 $cm^2/(\Omega$ equiv) (**4j**); 5.0×10^3, 95 (**4k**); 4.3×10^3, 93 (**4m**); 10.7×10^3, 109 (**4n**); 7.8×10^3, 114 (**4o**); 7.2×10^3, 120 (**4p**).

Reaction of 4a with Nucleophiles. (i) To a suspension of **4a** (500 mg, 0.89 mmol) in 5 mL of dry THF was added a THF solution (15 mL) of $NaCH(COMe)_2$ (0.89 mmol) at −19 °C under nitrogen. After the mixture was stirred for 30 min, the solvent was removed under vacuum, and the residual solids were extracted with diethyl ether. After the ether was removed, the solids were recrystallized from toluene–hexane to give orange crystals of $Pd(C_5H_5)(PPh_3)[CH_2CH_2CH(COMe)_2]\cdot{}^1/_2$(toluene): mp 94–95 °C dec; anal. ($C_{33.5}H_{35}O_2PPd$) C, H. The presence of a half molecule of toluene was also confirmed by ^1H NMR in $CDCl_3$: 5.67 (d, J_P = 1.4 Hz, Cp), 1.13 (m) and 1.78 (m) (CH_2CH_2), 1.91 (s, MeCO), 3.03 (t, J_H = 7.0 Hz, -CH<). The ethylene group resonances became two doublets of doublets in the spectra of the deuterio analogues prepared from the *cis*- or *trans*-ethylene-d_2 complex (see Figure 1): J_{gauche} = 4.2, J_{trans} = 12.3, J_P = 5.6, J_H = 7.0 Hz. (ii) To a dry CH_2Cl_2 solution (10 mL) of **4a** (200 mg, 0.35 mmol) was added slowly NaOMe (0.35 mmol) in methanol (1 mL) at −19 °C under nitrogen. The further procedure was almost identical with that described for obtaining **9**. $Pd(C_5H_5)(PPh_3)(CH_2CH_2OMe)$: orange-red crystals; mp 142–144 °C dec; anal. ($C_{26}H_{27}OPPd$) C, H; ^1H NMR ($CDCl_3$) δ 5.62 (d, J_P = 1.5 Hz, Cp), 1.40 (m, J_P = 5.6, J_{gem} = 9.3, J_{gauche} = 4.8, J_{trans} = 12.3 Hz, H^A), 3.20 (m, J_{gem} = 7.5 Hz, H^M), 2.97 (s, OMe). Similarly, $Pd(C_5H_5)(PPh_3)(CH_2CH_2O\text{-}i\text{-}Pr)$ (orange-red crystals, mp 75–77 °C) was obtained: anal. ($C_{28}H_{31}OPPd$) C, H; ^1H NMR ($CDCl_3$) δ 5.64 (d, J_P = 1.5 Hz, Cp), 1.44 (m, J_P = 5.6, J_{gem} = 8.9, J_{gauche} = 4.9, J_{trans} = 12.4 Hz, H^A), 3.21 (m, J_{gem} = 7.3 Hz, H^M), 0.92 (d, J_H = 6.0, Me), 3.25 (sept, OCH<). The magnitudes of these J_{gauche} and J_{trans} were also confirmed by the spectra of the deuterio analogues prepared from the ethylene-d_2 complex. (iii) When reactions of **4a** with diethylamine or pyridine were examined in $CDCl_3$ in NMR tubes at −50 °C, immediate disappearance of the absorptions of **4a** had occurred and instead new absorptions due to free ethylene (100%) and Cp protons of the amine complex (δ 5.78 for Et_2NH, δ 5.82 for py) appeared.

Preparation of 11. This was prepared from $Pd(C_5H_5)(PPh_3)(Br)$ and $TlCH(COMe)_2$ in THF at −19 °C and recrystallized from CH_2Cl_2–diethyl ether: orange crystals; mp 126 °C dec; anal. ($C_{28}H_{27}O_2PPd$) C, H; ^1H NMR ($CDCl_3$) δ 5.33 (d, J_P = 3.0 Hz, Cp), 2.30 (s, MeCO), 3.47 (d, J_P = 7.0 Hz, –CH<); IR (Nujol) 1620, 1650 cm^{-1} (CO).

Thermolysis of 9 and 10. Typically, in an NMR tube were weighed **9** (~0.02 mmol) and methyl β-naphthyl ether as reference, to which was added C_6D_6 (0.4 mL). The tube was then placed in the probe kept at 65 °C. After 30 min, yields of the products were measured by integrating the following absorptions against the reference peak: $CH_2{=}CHCH(COMe)_2$ (38%) δ 1.77 (s, MeCO), 4.67 (dd, J_{trans} = 17.3, J_{gem} = 1.5 Hz), and 4.96 (dd, J_{cis} = 10.5 Hz, $CH_2{=}$), 5.92 (dd, ═CH–); $CH_3CH{=}C(COMe)_2$ (27%) δ 1.40 (d, J_H = 7.5 Hz, $CH_3C{=}$), 1.74 (s) and 2.09 (s, MeCO), 5.94 (q, –CH═). The presence of C_5H_6 (ca. 25%) was confirmed by the multiplets at δ 2.68, 6.30, and 6.48. Ca. 30% of **9** still remained in the solution. Most of the 3-vinyl-2,4-pentanedione isomerized into 3-ethylidene-2,4-pentanedione when the mixture was kept at room temperature overnight. If the above thermolysis (65 °C, 30 min) was carried out either in a sealed tube under vacuum after deaeration through freeze–thaw cycles or in the presence of an equimolar quantity of free PPh_3, the β-hydrogen elimination was suppressed to as high as ca. 15%. Similarly, thermolyses (50 °C, 60 min) of **10a** in C_6D_6 gave methyl vinyl ether in 56% (conversion 60%, aerobic), 41% (44%, unaerobic), and 11% (22%, 1 equiv PPh_3 added) yields. On the other hand, the decomposition was almost complete within 15 min even at 23 °C (52% of 3-vinyl- and 25% of 3-ethylidene-2,4-pentanedione or 63% of methyl vinyl ether) when an equimolar amount of MCPBA was added to a benzene solution of **9** or **10a**.

Phosphine Exchange in 10a. Into an NMR tube containing known amounts of **10a** and PR_3 (R = C_6H_4OMe-*p*) ($[PR_3]/[\mathbf{10a}] \geq 7$) was added a known volume of C_6D_6 which had been kept at constant tem-

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[46] Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

[47] It remains to be established if the β-elimination also occurs from $Pd(\eta^1\text{-}C_5H_5)(PPh_3)(CH_2CH_2Y)$ to any significant extent.

[48] Winstein, S.; McCaskie, J.; Lee, H. B.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 6913.

[49] Linke, W. F. "Solubilities of Inorganic and Metal Organic Compounds"; American Chemical Society: Washington D.C., 1958, Vol. 1.

perature (23 °C). The tube was then placed in the probe at 23 °C, and the change in the ratio of the Cp proton resonances [δ 5.79 for **10a**, δ 5.92 for $Pd(C_5H_5)(PR_3)(CH_2CH_2OMe)$] was followed at appropriate intervals. Plots of log $[\mathbf{10a}]_t$ against time gave straight lines over 3 half-lives. From the pseudo-first-order rate constants, 4.0×10^{-3}, 6.8×10^{-3}, and 11.6×10^{-3} s^{-1} at $[PR_3] = 5.7 \times 10^{-2}$, 10.9×10^{-2}, and 15.3×10^{-2} M, respectively, $k_5 = (6.9 \pm 0.7) \times 10^{-2}$ M^{-1} s^{-1} was calculated. The equilibrium constant of eq 5 was found to be 3.8 ± 0.2 from equilibrium mixtures employing comparable concentrations of **10a** and PR_3.

Spectra. ^{1}H NMR spectra were measured on a JEOL PS-100 spectrometer equipped with a JNM-VT-3B variable-temperature controller, and ^{13}C NMR spectra on a JEOL FX-60 spectrometer, both with tetramethylsilane as internal reference. Except as specified, the spectra were taken at 23 °C. The spectra of the deuterio analogues of **9** and **10** were also taken at −50 °C to minimize the quadrupole-broadening effect of deuterium. To maintain temperature stability during the equilibrium measurements, we made little adjustments in gas-flow and spinning rates. The probe temperature was checked before and after each measurement by using the chemical shift of methanol on the basis of the calibration chart supplied from JEOL. Temperature stability was believed to be ±0.5 °C, and accuracy would be ±1 °C. IR spectra were obtained on a Hitachi 225 spectrophotometer.

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Substitution, Alkyl-Transfer, and Thermal-Decomposition Reactions of η^5-Cyclopentadienyl(triphenylphosphine)dimethylcobalt(III)

Eric R. Evitt and Robert G. Bergman*

Contribution from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and the Department of Chemistry, University of California, Berkeley, Berkeley, California 94720.

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Abstract: Reactions of $CpCo(PPh_3)(CH_3)_2$ (**1**, Cp = η^5-C_5H_5) with PMe_3, CO, PhC≡CPh and ethylene have been investigated in detail. PMe_3 replaces PPh_3 in **1** in a dissociative substitution reaction to give $CpCo(PMe_3)(Me)_2$; the first-order rate constant for PPh_3 loss from **1** is 4×10^{-4} s^{-1} at 30 °C in toluene-d_8. Dialkyl complex **1** doubly alkylates CO in an intramolecular process to give acetone in high yield; this proceeds via CO substitution in **1** to give the spectroscopically observed intermediate $CpCo(CO)(Me)_2$ (**6**), followed by migratory insertion and reductive elimination from an acyl–alkyl complex. Heating and then carbonylating mixtures of **1**-d_0 and **1**-d_6 (deuterated methyl groups) in benzene revealed the presence of an intermolecular methyl exchange process in **1**. We have reinvestigated the reaction of **1** with diphenylacetylene and, in addition to the organometallic products observed by previous workers, isolated two new organic products 2,3-diphenyl-1-butene (**11**) and (*Z*)-2,3-diphenyl-2-butene; these products account for >95% of the methyl groups in starting **1** and were formed in the ratio 14:1 in the absence of added PPh_3. Additional experiments designed to probe the mechanism of product formation led to the following conclusions: (1) high-yield stereospecific double alkylation of diphenylacetylene is a feasible process; (2) reactions of **11** in this system involve two diastereomeric η^2-olefin complexes which are interconvertible only by dissociation of the olefinic ligand from the metal; (3) hydrogen shifts involved in the $Cp(PPh_3)Co$-catalyzed isomerization of alkenes occur more rapidly than dissociation of the alkene from the metal center; and (4) interconversion of η^3-allyl complexes via rotation in σ^1-allyl complexes is much slower than hydrogen transfer and product formation. Ethylene reacts with **1** to give methane, propene, and the new ethylene complex $CpCo(PPh_3)(C_2H_4)$ (**14**); this was independently generated by thermal PPh_3 or photochemical CO substitution in $CpCo(PPh_3)_2$ and $CpCo(CO)(PPh_3)$, respectively. The production of propene from ethylene and **1** is a model for the chain-growth step in the Ziegler–Natta polymerization of olefins. Labeling experiments have shown propene is formed by transfer of one intact methyl group to ethylene, in agreement with a classical mechanism involving insertion of ethylene into a cobalt–carbon σ bond, rather than ethylene addition to an intermediate metal–carbene complex formed by β-elimination. Thermal decomposition of **1** is competitive with the alkylation of ethyene and gives mostly methane, abstracting the fourth methane hydrogen from the cyclopentadienyl ring. The decomposition has been monitored by ^{1}H NMR spectroscopy in the presence of added PPh_3 and ethylene (conditions where no propene is generated) and $Cp'Co(PPh_3)(C_2H_4)$ ($Cp' = \eta^5$-$CH_3C_5H_4$) and $Cp'Co(PPh_3)(Me)_2$ have been observed spectroscopically and identified as the primary and secondary products of the decomposition, respectively. Together, these reactions show reductive elimination in alkyl–acyl and alkyl–vinyl complexes is more favorable than alkyl–alkyl reductive elimination, and this is attributed to the ability of the former systems to donate an additional pair of electrons to the metal center in the reductive elimination transition state.

Introduction

The overall insertion of an unsaturated molecule into a transition metal–alkyl or hydride bond is one of the fundamental steps in organometallic reactions and often a primary process in reactions catalyzed by homogeneous solutions of transition-metal complexes.[1] The insertion of CO,[2] an alkyne,[3] or an alkene[4] into a metal–alkyl bond is of particular interest because it generates a new C–C bond. If a complex bearing two alkyl groups reacts in this way, two new C–C bonds can be formed. Insertion followed

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*Address correspondence to this author at the University of California, Berkeley.

[1] For reviews, see: (a) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 243–270; (b) Khan, M. M. T.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1964; Vols. I and II; (c) Heck, R. F. "Organotransition Metal Chemistry, A Mechanistic Approach"; Academic Press: New York, 1974; (d) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1979.

[2] For reviews, see: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145; (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311.