orthometalation,[1e,10,11,24] square-planar Pt ligand substitution,[25] and CO or alkane insertion into Pt–C bonds.[26] Several reference-laden reviews on orthometalation have also appeared.[10,12,24b]

Further elucidation of the mechanisms of orthometalation, dimerization, and ligand substitution at square-planar Pt may also be possible with these new data. Synthesis and reactions of ortho-metalated complexes are continuing to receive considerable attention at present.[21,27] Still other researchers will be interested, as we are, in the various modes of isomerism in ylid complexes[1d,e,12,28] such as ligand cis–trans isomerism, stereoisomers derived from the asymmetric C donor atom, Pt cis–trans isomerism, and ligand inequities resulting from steric crowding prior to orthometalation. Identification of these isomeric forms may lead to a recognition of which isomer is most important in the orthometalation process.

Acknowledgment. We wish to thank Dr. R. Harlow of E. I. duPont de Nemours, Wilmington, DE, for helpful discussions.

Registry No. 2, 86846-87-9; $Sn(APPY)(CH_3)_3Cl$, 38856-46-1; $PtCl_2$, 10025-65-7; APPY, 1439-36-7; $APPYH^+Cl^-$, 1235-21-8.

Supplementary Material Available: Tables and bonds and angles, anisotropic thermal parameters, hydrogen coordinates, and structure factors (24 pages). Ordering information is given on any current masthead page.

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(24) (a) Jones, C. E.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 992 (four-center intermediates). Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 558.

(25) Cf. Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stevenson, T. A.; Gould, R. O.; Alison, J. M. C.; Fraser, A. J. F. *Inorg. Chem.* **1982**, *21*, 2397.

(26) Cf. Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115. Chisholm, M. H.; Johns, W. S. *Inorg. Chem.* **1975**, *14*, 1189.

(27) McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523.

(28) Postal, M.; Pfeffer, M.; Riess, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 5623. Dehand, J.; Jordanov, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1553. Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F. *Ibid.* **1973**, 906. Powell, J.; Cooper, D. G. *J. Chem. Soc., Chem. Commun.* **1973**, 486.

Synthesis of (1,2,3,4-Tetramethylfulvene)palladium(0) Complexes from (η^5-Pentamethylcyclopentadienyl)palladium(II) Precursors. The Crystal Structure of [$Pd(PMe_3)_2(\eta^2\text{-}CH_2{=}C_5Me_4)$]

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[$Pd(\eta^3\text{-allyl})(\eta^5\text{-}C_5Me_5)$] complexes react with tertiary phosphines and phosphites in a stepwise manner to give initially (η^1-allyl)palladium complexes of the type [$PdL(\eta^1\text{-allyl})(\eta^5\text{-}C_5Me_5)$]. Reaction with a second ligand molecule leads to transfer of a hydrogen atom from a ring-methyl group to the allyl group to give the (tetramethylfulvene)palladium(0) complex [$PdL_2(\eta^2\text{-}CH_2{=}C_5Me_4)$]. The coordination of the fulvene molecule to the metal through the exo-methylene group has been established by an X-ray crystal structure determination of the trimethylphosphine adduct (space group $P2_1/a$, $a = 12.139$ (2) Å, $b = 13.468$ (2) Å, $c = 12.294$ (1) Å, $\beta = 105.874$ (8)°, $Z = 4$).

Introduction

In recent years the chemistry of organotransition-metal complexes containing the η^5-C_5Me_5 ring has received considerable attention. Maitlis in particular has shown that the substitution of the cyclopentadienyl hydrogen atoms by alkyl groups is frequently associated with a stabilization of the complexes formed by group 8 transition metals.[2]

Bercaw, Brintzinger, et al.[3] were the first to point out that the introduction of the C_5Me_5 group offers access to the 1,2,3,4-tetramethyl-5-methylene-1,3-cyclopentadiene (tetramethylfulvene) system and to suggest that [$Ti(\eta^5\text{-}C_5Me_5)_2$] undergoes a kinetically favored rearrangement to give a species (tentatively formulated as [$TiH(\eta\text{-}CH_2{=}C_5Me_4)(\eta^5\text{-}C_5Me_5)$]) in which a hydrogen atom has been transferred from a methyl group to the metal. Subsequently, Bottomley et al.[4] isolated a related complex, in which the $CH_2{=}C_5Me_4$ group bridges two titanium atoms, from the reaction of [$Ti(\eta^5\text{-}C_5Me_5)_2$] with N_2O and confirmed the structure by an X-ray analysis.

Our interest in this area stems from investigations on the reaction of [$Pd(\eta^3\text{-allyl})(\eta^5\text{-}C_5H_5)$] and [$Pd(\eta^3\text{-allyl})_2$] complexes with donor ligands.[5-8] We have shown that,

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(1) (a) University of Würzburg. (b) MPI für Kohlenforschung.

(2) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1.

(3) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. Bercaw, J. E. *Ibid.* **1974**, *96*, 5087. See also; McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629.

(4) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

(5) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155.

(6) Werner, H.; Kühn, A.; Tune, D. J.; Krüger, C.; Brauer, D. J.; Sekutowski, J. C.; Tsay, Y.-H. *Chem. Ber.* **1977**, *110*, 1763. Kühn, A.; Werner, H. *J. Organomet. Chem.* **1979**, *179*, 421. Werner, H.; Kühn, A. *Ibid.* **1979**, *179*, 439. Werner, H. *Ibid.* **1980**, *200*, 235.

(7) Werner, H.; Kühn, A.; Burschka, C.. *Chem. Ber.* **1980**, *113*, 2291. Kühn, A.; Werner, H. *Ibid.* **1980**, *113*, 2308. Werner, H.; Kühn, A. *Angew. Chem.* **1979**, *91*, 447; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 416. Tune, D. J.; Werner, H. *Helv. Chim. Acta* **1975**, *58*, 2240.

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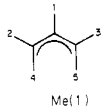
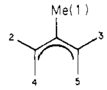
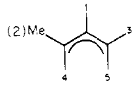
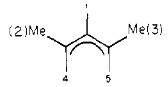
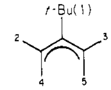
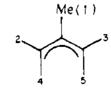
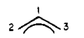
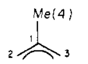
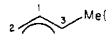
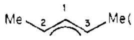
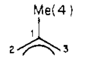
Table I. ^{1}H NMR Spectral Data for the [Pd(η^3-allyl)(η^5-C_5Me_5)] Complexes[a,b]

complex	η^3-allyl group	$\delta(H_1)$	$\delta(H_2)$	$\delta(H_3)$	$\delta(H_4)$	$\delta(H_5)$	$\delta(H_{CpMe})$	$J_{H,H}$, Hz
3		4.75 (m)	2.96 (d)		1.91 (d)		2.10 (s)	$J_{1,2}$ = 6.1, $J_{1,4}$ = 10.7
4		1.71 (s)	2.79 (s)		2.02 (s)		2.08 (s)	
5		4.48 (m)	1.19 (d)	2.94 (d)	2.58 (m)	1.96 (d)	2.06 (s)	$J_{1,3}$ = 6.1, $J_{1,5}$ = 10.4, $J_{1,4}$ = 9.6, $J_{2,4}$ = 6.3, $J_{4,5}$ = 0.7
6		4.16 (t)	1.17 (d)		2.53 (m)		2.00 (s)	$J_{2,4}$ = 6.0, $J_{1,4}$ = 9.0
7		1.00 (s)	3.00 (s)		1.85 (s)		2.10 (s)	
8[c]		1.67 (s)	2.81 (s)		2.01 (s)		c	

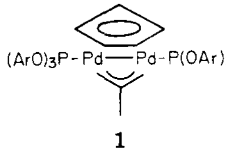
[a] Spectra measured in toluene-d_8 at −60 °C. [b] Multiplicity: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; br, broad. [c] [Pd(η^3-2-MeC_3H_4)(η^5-C_5Me_4Et)] (**8**). $\delta(H_{CpMe})$ 2.03 (s), 2.05 (s); $\delta(H_{CpEt})$ 1.07 (t), 2.40 (q), J = 7.0 Hz.

Table II. $^{13}C\{^1H\}$ NMR Spectral Data for the [Pd(η^3-allyl)(η^5-C_5Me_5)] Complexes[a]

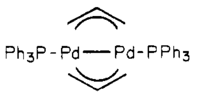
complex	η^3-allyl group	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_4)$	$\delta(C_{Cp})$	$\delta(C_{CpMe})$	$^1J_{C,H}$, Hz
3		95.6	44.60			104.7	11.5	$J_{C_1,H}$ = 162, $J_{C_2,H}$ = 164, $J_{Me_{Cp},H}$ = 126
4		109.1	44.9		22.9	104.4	11.3	$J_{C_2,H}$ = 152, $J_{Me_{Cp},H}$ = 126
5		96.5	43.4	59.6	17.7	103.9	11.0	$J_{C_1,H}$ = 161, $J_{C_2,H}$ = 157, $J_{C_3,H}$ = 156, $J_{C_4,H}$ = 126, $J_{Me_{Cp},H}$ = 126
6		97.4	58.6		18.1	103.0	10.7	$J_{C_1,H}$ = 159, $J_{C_2,H}$ = 156, $J_{C_4,H}$ = 126, $J_{Me_{Cp},H}$ = 125
8[b]		109.1	45.0		23.1	b	b	$J_{C_2,H}$ = 157, $J_{C_4,H}$ = 127

[a] Spectra measured in toluene-d_8. [b] [Pd(η^3-2-MeC_3H_4)(η^5-C_5Me_4Et)]. $\delta(C_{Cp})$ 103.7, 104.3, 112.2; $\delta(C_{CpMe})$ 11.3, 11.1; $\delta(C_{CpEt})$ 18.9, 19.1; $J_{Me_{Cp},H}$ = 126, $J_{Et_{Cp},H}$ = 126 Hz.

depending upon the ligand, the initial reaction is that of addition with rearrangement of the allyl or cyclopentadienyl group to give complexes of the type [PdL(η^1-allyl)(η^5-C_5H_5)], [PdL(η^1-C_5H_5)(η^3-allyl)], or [PdL(η^1,η^3-allyl)$_2$]. These adducts can react further to give binuclear species having bridging allyl or cyclopentadienyl groups, e.g., **1** and **2**.



1



2

We report here the extension of this work to systems containing the η^5-C_5Me_5 group and the discovery of an unexpectedly facile hydrogen-transfer reaction that leads to the generation of the first (fulvene)palladium(0) complexes. A preliminary account has been published.[9]

Results and Discussion

The (pentamethylcyclopentadienyl)palladium complexes [Pd(η^3-allyl)(η^5-C_5Me_5)] **3**–**7** listed in the tables have been prepared by reacting the appropriate [PdCl(η^3-allyl)]$_2$ dimer with LiC_5Me_5 in a manner analogous to that used to prepare the corresponding cyclopentadienylpalladium complexes (e.g., eq 1).[10] [Pd(η^3-2-MeC_3H_4)(η^5-C_5Me_4Et)] (**8**) was prepared similarly from a reaction with LiC_5Me_4Et.

$$[\mathrm{PdCl}(\eta^3\text{-allyl})]_2 + 2\mathrm{LiC_5Me_5} \xrightarrow{-2\mathrm{LiCl}} 2[\mathrm{Pd}(\eta^3\text{-allyl})(\eta^5\text{-C_5Me_5})] \quad (1)$$

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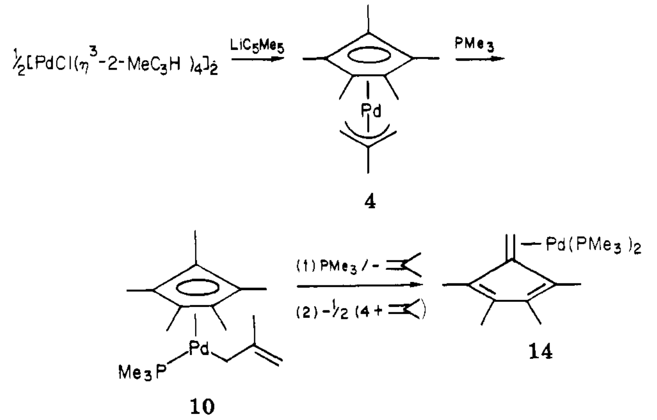
(8) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449. Jolly, P. W.; Krüger, C.; Schick, K.-P.; Wilke, G. *Z. Naturforsch., Anorg. Chem. Org. Chem.* **1981**, *35B*, 926.

(9) Kraus, H.-J.; Werner, H. *Angew. Chem.* **1982**, *94*, 871; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 866; *Angew. Chem., Suppl.* **1982**, 1793.

(10) See: Fischer, E. O.; Werner, H. "Metal π-Complexes"; Elsevier: Amsterdam, London, New York, 1966; Vol. 1, Chapter VI.

Scheme I



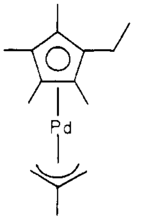
Complexes **3**–**8** are air-sensitive, dark-red to purple, low-melting, crystalline solids that are soluble in all common organic solvents and have been characterized by their ^{1}H and ^{13}C NMR spectra (Tables I and II). The NMR spectra have been compared with those of the analogous [Ni(η^3-allyl)(η^5-C_5H_5)] complexes.[11,12] The ^{1}H NMR spectra of the η^3-1-MeC_3H_4 and η^3-1,3-$Me_2C_3H_3$ complexes **5** and **6** respectively, indicate that the methyl groups adopt the expected syn positions ($J_{1,4}$ = 9.6 and 9.0 Hz, respectively). The gated-decoupled ^{13}C NMR spectra have enabled a complete assignment to be made, and the chemical shifts and ^{13}C–^{1}H coupling constants are comparable to those found in the nickel complexes.

The further reaction with donor ligands was originally explored in the hope of isolating bimetallic complexes of the type [Pd_2L_2(μ-allyl)(μ-C_5Me_5)]. The reaction with PMe_3 occurs in a stepwise manner. Additon of 1 equiv of the phosphine to a toluene solution of [Pd(η^3-2-MeC_3H_4)(η^5-C_5Me_5)] at −60 °C leads to the formation of an adduct (**10**) in which the η^3-allyl group has been converted into the η^1-form (Scheme I). Treatment of **10** with a second equivalent of PMe_3 and warming the solution up to 0 °C results in the elimination of isobutene (^{1}H NMR) and formation of a bis(phosphine)palladium species (**14**) for which spectroscopic and chemical evidence indicate that a tetramethylfulvene molecule is π-bonded to the metal through the exo-methylene group. **14** can of course be prepared in a one-pot reaction (in 80–90% yield) by reacting the starting material **4** with 2 equiv of trimethylphosphine at room temperature in pentane. It is also the product of a disproportionation reaction that occurs quantitatively (^{1}H and ^{31}P NMR spectra) upon allowing a solution of **10** to warm up from −60 to 0 °C.

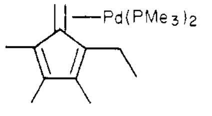
The fulvene complex **14** is a bright yellow, air-sensitive solid which in the crystalline state is stable at room temperature. The ^{31}P{^{1}H} NMR spectrum consists of an AB quartet ($J_{P,P}$ = 28.3 Hz in acetone-d_6 at −10 °C) indicative of two nonequivalent phosphorus nuclei in a cis arrangement. The low-temperature ^{1}H NMR spectrum shows the palladium to be coordinated to the exo-methylene group of the tetramethylfulvene molecule ($\Delta\delta$(CH_2=CR_2) 2.0 and 2.5 with respect to free fulvene). At room temperature the signals for both the exo-methylenic hydrogen atoms, the methyl groups and the phosphorus atom broaden. Preliminary results suggest that this effect may well be due to ligand dissociation; experiments in which PMe_3 and PEt_3 were added in a stepwise manner led to the formation of all four possible (fulvene)PdL_2 isomers. The low-temperature ^{13}C{^{1}H} NMR spectrum in acetone-d_6 at −25 °C has signals at 35.8 and 88.8 ppm that are assigned to the complexed C atoms. These signals appear as a doublet of doublets due to coupling with the two nonequivalent P atoms. Gated-decoupled spectra show the expected triplet for the exo-methylenic C atom with a typical coupling constant $^1J_{C,H}$ of 162 Hz. The structure of **14** has been confirmed by the X-ray structural determination that is described in the following section.

The reactions described above involving PMe_3 are not limited to the η^3-2-MeC_3H_4 palladium complex **4**, and a series of complexes containing the η^1-allyl group and related to **10** has been characterized. The spectroscopic data for the resulting complexes **9**–**12** as well as [Pd(PMe_3)(η^1-2-MeC_3H_4)(η^5-C_5Me_4Et)] (**13**) are shown in Tables III and IV. The ^{1}H NMR data of the complexes containing the η^1-3-MeC_3H_4 and η^1-1,3-$Me_2C_3H_3$ groups (**11** and **12**, respectively) are consistent with an E configuration of the double bond ($J_{1,5} \approx$ 15 Hz). The ^{13}C NMR spectra have been compared to those of the related ruthenium complexes [Ru(PPh_3)$_2$(η^1-allyl)(η^5-C_5H_5)]:[12] the P atom couples to both the metal-bonded C atom of the η^1-allyl group ($J_{P,C}$ = 7–10 Hz) and the ring carbon atoms ($J_{P,C}$ = 2–3 Hz).

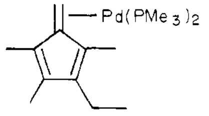
As expected, the monophosphine complexes **9**–**12** react with a second PMe_3 molecule to give the fulvene complex **14**. Addition of a second equivalent of PMe_3 to the tetramethylethylcyclopentadienyl derivative **8** results in the formation of a mixture of the two fulvene isomers **15** and **16** in a ratio of 3:2 (^{31}P, ^{1}H NMR). Interestingly, hydrogen transfer from the ethyl group, which would lead to a complex containing a π-bonded MeCH=C_5Me_4 molecule, is not observed.



8



15



16

Ligands other than trimethylphosphine react similarly, and the bis(ligand)palladium fulvene complexes **17**–**19** have been isolated from reactions involving PEt_3, P(OMe)$_3$, and $Cy_2PC_2H_4PCy_2$ (Cy = cyclohexyl). In the case of the fulvene complexes **17**–**19** the exo-methylenic protons appear in the ^{1}H NMR spectra as the expected doublet of doublets due to coupling with the two magnetically inequivalent phosphorus atoms. The spectroscopic data for the fulvene complexes have been brought together in Tables V and VI.

Although a complete, systematic investigation has not been attempted, the nature of the substituents on the allyl group in the [Pd(η^3-allyl)(η^5-C_5Me_5)] complexes appears to effect its reactivity with ligands. Thus although no reaction is observed on treating [Pd(η^3-2-t-BuC_3H_4)(η^5-C_5Me_5)] with PPh_3 or P-i-Pr_3 at 50–60 °C in toluene, the η^3-C_3H_5 and η^3-2-MeC_3H_4 analogues **3** and **4** react with both P-i-Pr_3 and PCy_3 at room temperature to give (among others) the expected (fulvene)palladium bis(ligand) complexes (δ(^{31}P) 44.5 (d), 34.3 (d), $J_{P,P}$ = 19.4 Hz for the P-i-Pr_3 complex; δ(^{31}P) 32.5 (d) 28.1 (d), $J_{P,P}$ = 21.4 Hz for the PCy_3 complex). This also accounts for the observation that the reaction of the η^3-2-t-BuC_3H_4 complex with PPh_2Me or PMe_2Ph occurs only at 60 °C, at which tem-

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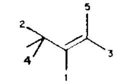
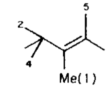
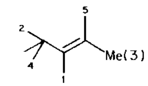
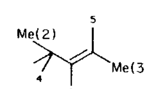
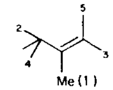
(11) Benn, R.; Schroth, G. *Org. Magn. Reson.* **1980**, *14*, 435. Benn, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1054. Lehmkuhl, H.; Rufińska, A.; Mehler, K.; Benn, R.; Schroth, G. *Justus Liebigs Ann. Chem.* **1980**, 744.

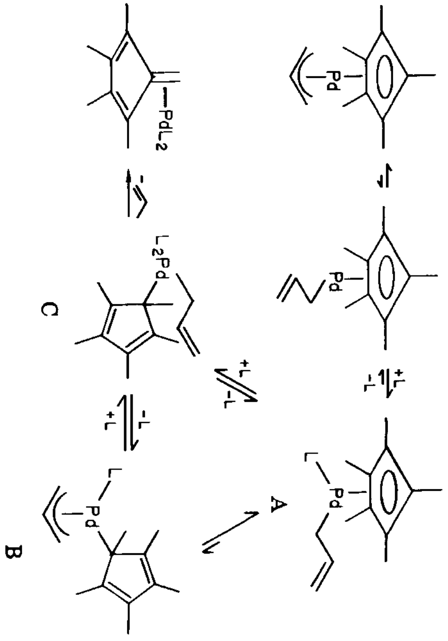
(12) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

Table III. ^1H and ^{31}P NMR Spectral Data for the $[Pd(PMe_3)(\eta^1\text{-allyl})(\eta^5\text{-}C_5Me_5)]$ Complexes[a,b]

complex	η^1-allyl group	$\delta(H_1)$	$\delta(H_2)$	$\delta(H_3)$	$\delta(H_4)$	$\delta(H_5)$	$\delta(H_{CpMe})$	$\delta(H_{PMe})$	$J_{H,H}$, Hz	$\delta(^{31}P)$[c]
9		6.15 (sx)	nd[d]	4.7 (d)	nd[d]	5.0 (d)	1.94 (d)	0.83 (d)	$J_{1,3} = 9, J_{1,5} = 17,$ $J_{P,CMe} = 2, J_{PMe} = 9$	−12.1 (s)
10		1.91 (d)	2.10 (m)	4.69 (m)	2.10 (m)	4.84 (d)	1.92 (d)	0.85 (d)	$J_{1,3} = 1.4, J_{3,5} = 3.2,$ $J_{2,5} = 0.9, J_{P,2} = 4.8,$ $J_{P,CMe} = 2.3, J_{PMe} = 9.4$	−13.6 (s)
11		5.84 (m)	2.10 (m)	1.81 (d)	2.10 (n)	5.44 (n)	1.99 (d)	0.79 (d)	$J_{1,2} = 8.5, J_{1,5} = 14.7,$ $J_{3,5} = 6.5, J_{1,3} = -1.6,$ $J_{P,CMe} = 2.2, J_{P,Me} = 9.3$	−13.4 (s)
12		5.94 (dd)	1.41 (d)	1.90 (d)	2.33 (m)	5.23 (m)	1.92 (d)	0.72 (d)	$J_{1,5} = 5.2, J_{3,5} = 6.5,$ $J_{1,4} = 5.6, J_{1,3} = -1,8,$ $J_{2,4} = 6.9, J_{4,5} = -1.9,$ $J_{4,P} \approx 11.4, J_{2,P} = 1.9,$ $J_{P,CMe} = 2.2, J_{PMe} = 9.0$	−12.7 (s)
13[e]		1.92 (d)	2.13 (m)	4.72 (br)	2.13 (m)	4.90 (br)	*e*	0.77 (d)	$J_{3,5} = 3.1, J_{2,P} = 4.6,$ $J_{5,P} = 1.3, J_{P,Me} = 9.5$	−13.9

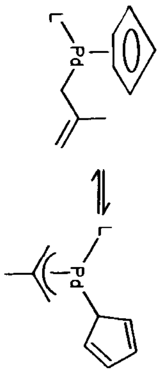
[a] Spectra measured in toluene-d_8 at −60 °C. [b] Multiplicity, see Table I. [c] ^{31}P chemical shifts are referenced to external 85% H_3PO_4. [d] Resonances probably fall under those for the C_5Me_5 group. [e] $[Pd(PMe_3)(\eta^1\text{-}2\text{-}MeC_3H_4)(\eta^5\text{-}C_5Me_4Et)]$ (13). $\delta(H_{CpMe})$ 1.89 (d), 1.91 (d), $J_{P,H}$ = 2.2, 2.5 Hz; $\delta(H_{CpEt})$ 1.08 (t), 2.30 (q), $J_{H,H}$ = 7.5 Hz.

Scheme II



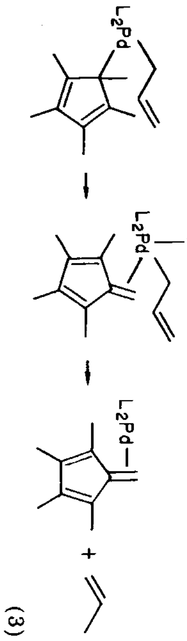
perature the tetrakis(ligand)palladium complex is formed.

A plausible mechanism for the reactions described here is shown in Scheme II. The reaction with 1 equiv of ligand to give the η^1-allyl species A and the subsequent disproportionation have been established in this publication. The equilibrium between A and B is not detectable in the NMR spectra but does have precedence in the $[Pd(\eta^3\text{-allyl})(\eta\text{-}C_5H_5)]$/L system (eq 2).[7] The further reaction sequence is more speculative. One possibility is the reaction with a second ligand molecule to give the $[PdR_2L_2]$ species C that can exist in either a cis or trans form. Whether the transition state for the further reaction involves a trigonal, tetrahedral, or square-planar species is not known.



(2)

The final step that leads to formation of the fulvene presumably occurs by transfer of a β-hydrogen atom from an η^1-C_5Me_5 moiety to the metal and subsequently to the η^1-allyl group (eq 3). Alternatively one can visualize the direct transfer of a hydrogen atom from a ring-methyl group to the allyl group in either species A or C. It is perhaps relevant to mention that $[PdL_2(\eta^1\text{-allyl})_2]$ complexes have been isolated from reaction of bis(η^3-allyl)palladium complexes with phosphines.[13] Yamamoto et al.[14] have shown that the products of the thermolysis of $[PdEt_2L_2]$ complexes depends upon their geometry: the cis isomer gives mainly butane as the result of reductive coupling of the ethyl groups while the trans isomer gives the 1:1 mixture of ethane and ethylene expected for a β-hydrogen-transfer process.



(3)

The tetramethylfulvene molecule is displaced from the metal atom upon reacting the complex 14 with methyl iodide,[15] thiophenol, and dimethyl acetylenedicarboxylate

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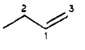
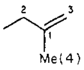
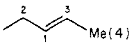
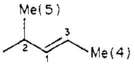
(13) Jolly, P. W.; Joswig, T.; Krüger, C., unpublished results (1982).

(14) Ozawa, F.; Ito, T.; Yamamoto, L. *J. Am. Chem. Soc.* **1980**, *102*, 6457. Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.

Table IV. $^{13}C\{^1H\}$ NMR Spectral Data for the [Pd(PMe_3)(η^1-allyl)(η^5-C_5Me_5)] Complexes[a]

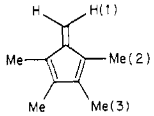
complex	η^1-allyl group	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_4)$	$\delta(C_{Cp})$	$\delta(C_{CpMe})$	δ(PMe)	$^1J_{C,H}$, $J_{P,C}$, Hz
9		145.1	14.1 (d)	103.4		104.4 (d)	10.6	15.2 (d)	$J_{P,C_2} = 9.2$, $J_{P,C_{Cp}} = 3.1$, $J_{P,Me} = 27.5$
10		154.1 (d)	16.6 (d)	102.7	26.3	104.4 (d)	10.7	15.1 (d)	$J_{P,C_1} = 1.2$, $J_{P,C_2} = 10.5$, $J_{P,Cp} = 2.8$, $J_{P,Me} = 27.3$, $J_{C_3,H} = 154$, $J_{C_4,H} = 131$, $J_{Me_{Cp},H} = 126$
11		138.5	12.5 (d)	112.7	19.2	104.3 (d)	10.7	15.5 (d)	$J_{P,C_2} = 10.2$, $J_{P,Cp} = 2.0$, $J_{P,Me} = 26.5$, $J_{C_1,H} = 146$, $J_{C_3,H} = 147$, $J_{ME_{Cp},H} = 125$
12		141.5	19.5 (d)	109.4	19.2[b]	104.5 (d)	10.6	15.3 (d)	$J_{P,C_2} = 7.1$, $J_{P,Cp} = 2.0$, $J_{P,Me} = 26.5$, $J_{C_1,H} = 143$, $J_{C_3,H} = 148$, $J_{Me_{Cp},H} = 125$

[a] Spectra measured in toluene-d_8 at −60 °C. [b] $\delta(C_5)$ 21.3.

Table V. ^1H and ^{31}P NMR Spectral Data for the [PdL_2(η^2-$CH_2{=}C_5Me_4$)] Complexes[a]

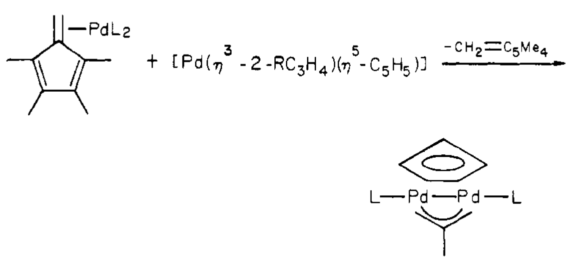
complex	L	$\delta(H_1)$	$\delta(H_2)$	$\delta(H_3)$	$\delta(H_L)$	$\delta(^{31}P)$	$J_{P,H}$, $J_{P,P}$, Hz
14[b]	PMe_3	2.89 (t)[c]	2.06 (d)	1.98 (br)	0.70 (d) 0.92 (d)	−23.4 (d) −24.9 (d)	$\Sigma J_{P,H_1/H_2} = 10.6$, $J_{P,Me} = 5.5$, $J_{P,P} = 34.8$
17[d]	PEt_3	2.53 (dd)	1.80 (d)	1.70 (br)	0.95 (m) 1.18 (m)	8.11 (d) 16.52 (d)	$J_{P,H_1} = 5.0, 7.0$, $J_{P,H_2} = 4.0$, $J_{P,P} = 16.4$
18[d]	$P(OMe)_3$	3.04 (dd)	1.80 (d)	1.70 (br)	3.28 (d) 3.56 (d)	152.34 (d) 155.00 (d)	$J_{P,H_1} = 8.0, 8.0$, $J_{P,H_2} = 6.0$, $J_{P,Me} = 12.0$, $J_{P,P} = 25.3$
19[e]	$Cy_2PC_2H_4PCy_2$	3.18 (dd)	2.05 (br)		0.6–1.6 (br)	48.6 (d) 55.8 (d)	$J_{P,H_1} = 4.5, 7.0$, $J_{P,P} = 26.9$
15[b,f,g]	PMe_3	2.9 (m)	2.1–2.2		0.69 (d) 0.93 (d)	−23.6 (d) −26.2 (d)	$J_{P,Me} = 5.9, 6.3$, $J_{P,P} = 31.4$
16[b,f,h]	PMe_3	2.9 (m)	2.1–2.2		0.75 (d) 0.94 (d)	−23.0 (d) −25.9 (d)	$J_{P,Me} = 5.9, 6.4$, $J_{P,P} = 33.3$

[a] Multiplicity, see Table I.



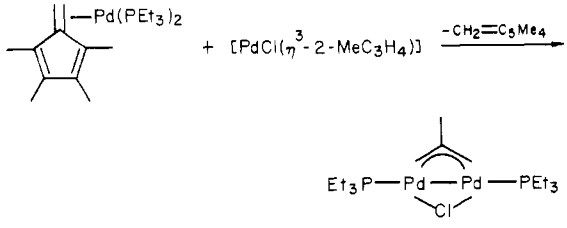
[b] Toluene-d_8, −60 °C. [c] $\delta(H_1)$ 2.54 (dd, $J_{P,H}$ = 5 and 6 Hz) in acetone-d_6 at −10 °C. [d] Acetone-d_6, −20 °C. [e] Toluene-d_8, +30 °C. [f] These assignments could be reversed. [g] $\delta(H_{CH_2CH_3})$ 1.24 (t, $J_{H,H}$ = 7.4 Hz); $\delta(H_{CH_2CH_3})$ 2.25 (m), 2.56 (m), $J_{H,H}$ = 7.4, −13.7 Hz. [h] $\delta(H_{CH_2CH_3})$ 1.30 (t, $J_{H,H}$ 7.5 Hz, $\delta(H_{CH_2CH_3})$ 2.53 (m), 2.63 (m), $J_{H,H}$ = 7.5, −13.6 Hz.

(Scheme III) as well as in the reactions with [Pd(η^3-2-RC_3H_4)(η-C_5H_5)] and [PdCl(η^3-2-MeC_3H_4)]$_2$ (eq 4 and 5).



(4)

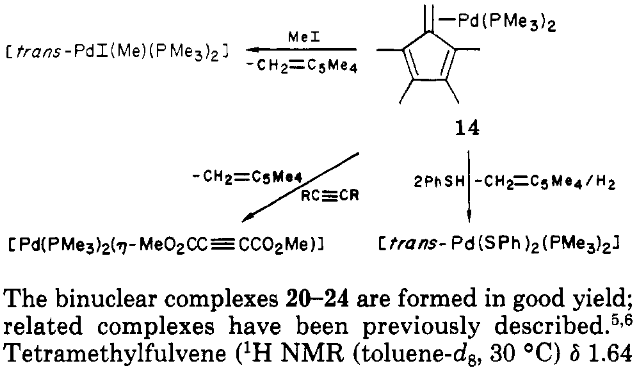
20, R = Me, L = PMe_3
21, R = Me, L = PEt_3
22, R = Me, L = $P(OMe)_3$
23, R = t-Bu, L = PEt_3



(5)

24

Scheme III



The binuclear complexes **20**–**24** are formed in good yield; related complexes have been previously described.[5,6] Tetramethylfulvene (^1H NMR (toluene-d_8, 30 °C) δ 1.64 (s), 1.78 (s), Me; δ 5.28 (s), $=CH_2$) can be isolated as a yellow distillable liquid from these reactions. This compound was first reported in 1981 as one of the products of the photolysis of pentamethylcyclopentadiene.[23]

The Crystal Structure of [Pd(PMe_3)$_2$(η^2-$CH_2{=}C_5Me_4$)] (14). The fulvene molecule can interact with a metal atom in a variety of ways, and complexes have been reported in which it bonds as an η^2- or η^4-organic ligand

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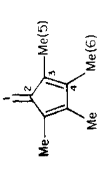
(15) Werner, H.; Bertleff, W. *J. Chem. Res., Miniprint* **1978**, *2720*; *J. Chem. Res., Synop.* **1978**, 201.

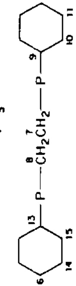
Table VI. ^{13}C NMR Spectral Data for the $[PdL_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ Complexes[a, b]

complex	L	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_4)$	$\delta(C_5)$	$\delta(C_6)$	$\delta(C_L)$	$J_{P,C}$, $^1J_{C,H}$, Hz
14	PMe_3	35.8 (dd)	88.8 (dd)	127.3 (d)	124.1 (d)	11.6 (d)	11.5 (s)	20.0 (dd) 16.3 (d)	$J_{P,C_1} = 29.9, 2.8, J_{P,C_2} = 15.8, 3.4$ $J_{P,C_3} = 5.1, J_{P,C_4} = 3.4, J_{P,C_5} = 5.2, J_{P,Me} = 16.9, 2.9, J_{P',Me} = 14.7, J_{C_1,H} = 162$
17	PEt_3	37.5 (dd)	90.2 (dd)	128.0 (dd)	125.3 (d)	11.7 (d)	11.6 (s)	20.8 (dd), 9.0 (d) 16.1 (d), 8.9 (d)	$J_{P,C_1} = 21.5, 4.4, J_{P,C_2} = 18.4, 4.4$ $J_{P,C_3} = 5.2, 2.2, J_{P,C_4} = 3.7, J_{P,C_5} = 2.2, J_{P,CH_2} = 14.0, 2.9, J_{P,Me} = 17.7, J_{P',CH_2} = 12.5, J_{P',Me} = 17.7, J_{C_1,H} = 155$
18	$P(OMe)_3$	43.6 (dd)	93.8 (dd)	129.3 (d)	129.1 (d)	11.6 (d)	11.5 (s)	93.68 (dd) 50.3 (d)	$J_{P,C_1} = 30.9, 6.6, J_{P,C_2} = 19.9, 5.2$ $J_{P,C_3} = 11.8, J_{P,C_4} = 8.8, J_{P,C_5} = 2.9, J_{P,Me} = 19.9, 5.2, J_{P',Me} = 18.0, 4.1, J_{C_1,H} = 159$
19[c]	$Cy_2PC_2H_4PCy_2$	37.3 (dd)	89.7 (dd)	128.4 (dd)	126.00 (dd)	12.0 (d)	12.3 (d)	*d*	$J_{P,C_1} = 30.5, 2.5, J_{P,C_2} = 15.8, 4.1, J_{P,C_3} = 6.1, 2.0, J_{P,C_4} = 4.1, 1.0, J_{P,C_5} = 2.3, J_{C_1,H} = 153$

[a] Multiplicity, see Table I.



[b] Acetone-d_6 at −50 °C (14), −26 °C (17), and −26 °C (18). [c] Toluene-d_8 at 30 °C. [d]



$\delta(C_{7,8})$ 21.6, 23.7 (dd), $\delta(C_{9,13})$ 35.5, 36.0 (dd), $\delta(C_{10,14})$ 30.6, 28.9 (d), $\delta(C_{11,15})$ 27.8, 27.6 (d), $\delta(C_{12,16})$ 26.9, 26.8 (d), $J_{P,C_7} = 19.3, 17.2$, $J_{P,C_8} = 18.0, 17.5$, $J_{P,C_9} = 8.9, 3.7$, $J_{P,C_{13}} = 8.9, 2.9$, $J_{P,C_{10}} = 8.4$, $J_{P,C_{14}} = 8.1$, $J_{P,C_{11}} = 13.1$, $J_{P,C_{15}} = 13.1$, $J_{P,C_{12}} = 1.2$, $J_{P,C_{16}} = 0.9$ Hz.

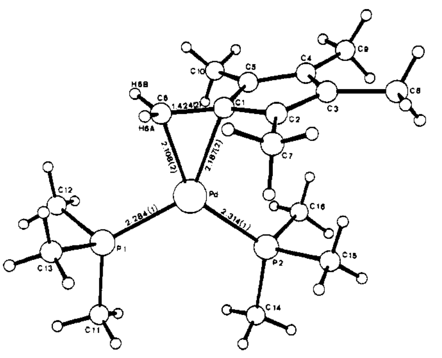


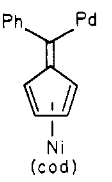
Figure 1. The structure of $[Pd(PMe_3)_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ (14).

Table VII. Bond Lengths (Å) in $[Pd(PMe_3)_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ (14)[a]

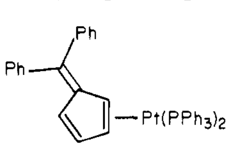
Pd-P1	2.284 (1)	C2-C7	1.498 (2)
Pd-P2	2.314 (1)	C3-C8	1.503 (3)
Pd-C1	2.187 (2)	C4-C9	1.505 (3)
Pd-C6	2.108 (2)	C5-C10	1.499 (3)
C1-C6	1.424 (2)	P1-C11	1.830 (2)
C1-C5	1.469 (2)	P1-C12	1.823 (2)
C1-C2	1.472 (2)	P1-C13	1.829 (2)
C2-C3	1.367 (2)	P2-C14	1.836 (2)
C3-C4	1.462 (2)	P2-C15	1.832 (2)
C4-C5	1.365 (2)	P2-C16	1.827 (2)

[a] Esds in parentheses.

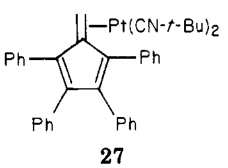
or in which it adopts an η^5-cyclopentadienyl arrangement.[16,17] Although complexes involving nickel and platinum are known, no previous palladium fulvene complexes have been reported. The nickel complexes were originally isolated over a decade ago,[18] and the substituted fulvene molecule has subsequently been shown to be complexed as an η^4-organic ligand, e.g., **25**.[19] In the case of platinum, the fulvene complexes as an η^2-alkene, either through a ring double bond, e.g., **26**, or through the exo-methylene group, e.g., **27**.[17] X-ray diffraction studies have confirmed the structures of **25** and **26**. In addition to the platinum and palladium complexes, complexation through the exo-methylene group has been observed in fulvene complexes of rhodium[20] and manganese.[21]



25



26



27

A single-crystal X-ray structural determination was undertaken to establish the bonding situation of **14**. The molecular arrangement is shown in Figure 1, and a list of important bond lengths and angles are to be found in Tables VII and VIII. Details of the determination have been included in the Experimental Section.

The palladium atom in **14** lies in a trigonal-planar environment interacting with the two phosphorus atoms P1 and P2 and the exocyclic double bond (C1 and C6). The

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(16) Watts, W. E. *J. Organomet. Chem.* **1981**, *220*, 165.

(17) Christofides, A.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Organomet. Chem.* **1982**, *232*, 279.

(18) Englert, E. Doctoral Thesis, University of Bochum, 1971.

(19) Edelmann, F.; Lubke, B.; Behrens, U. *Chem. Ber.* **1982**, *115*, 1325.

(20) Altmann, J.; Wilkinson, G. *J. Chem. Soc.* **1964**, 5654.

(21) Edelmann, F.; Behrens, U. *J. Organomet. Chem.* **1977**, *128*, 131.

Table VIII. Bond Angles in $[Pd(PMe_3)_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ (14)[a]

C6-Pd-C1	38.7 (1)	C6-C1-C5	126.2 (2)
C6-Pd-P1	98.7 (1)	C1-C2-C7	123.8 (2)
C6-Pd-P2	146.2 (1)	C3-C2-C7	128.4 (2)
C1-Pd-P1	137.3 (1)	C2-C3-C8	127.4 (2)
C1-Pd-P2	107.6 (1)	C8-C3-C4	123.5 (2)
P1-Pd-P2	115.1 (1)	C3-C4-C9	123.0 (2)
C5-C1-C2	106.3 (1)	C9-C4-C5	127.9 (2)
C1-C2-C3	107.7 (1)	C4-C5-C10	128.1 (2)
C2-C3-C4	109.0 (1)	C10-C5-C1	124.1 (2)
C3-C4-C5	109.1 (1)	C12-P1-C13	101.2 (1)
C4-C5-C1	107.9 (1)	C11-P1-C12	101.5 (1)
C1-C6-Pd	73.7 (1)	C11-P1-C13	100.3 (1)
Pd-C6-H6A	111.0 (13)	C11-P1-Pd	121.5 (1)
Pd-C6-H6B	113.2 (14)	C12-P1-Pd	113.2 (1)
C1-C6-H6A	117.9 (14)	C13-P1-Pd	116.2 (1)
C1-C6-H6B	116.9 (15)	C16-P2-C15	100.5 (1)
H6A-C6-H6B	116.4 (20)	C14-P2-C15	101.8 (1)
C6-C1-C2	125.9 (2)	C14-P2-C16	101.7 (1)
C6-C1-Pd	67.6 (1)	C14-P2-Pd	121.6 (1)
Pd-C1-C2	107.9 (1)	C15-P2-Pd	113.9 (1)
Pd-C1-C5	110.6 (1)	C16-P2-Pd	114.5 (1)

[a] Esds in parentheses.

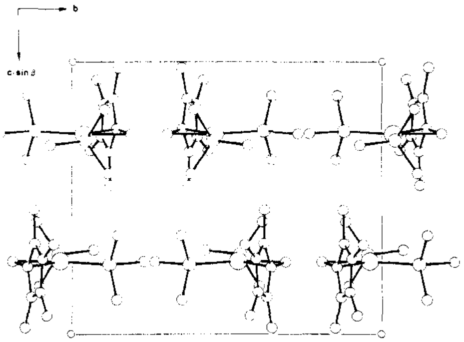

Figure 2. The unit cell in crystalline **14** projected along the *a* axis.

maximum deviation from planarity is 0.03 Å which corresponds to a dihedral angle of 2.8° between the planes defined by Pd,P1,P2 and Pd,C1,C6. There is clearly no interaction between the metal and the other ring-carbon atoms (Pd–C2 = 2.987 (2) Å, Pd–C3 = 3.891 (2) Å, Pd–C4 = 3.917 (2) Å, and Pd–C5 = 3.034 (2) Å). Coordination causes an elongation of the bond C1–C6 to 1.424 (2) Å which is a value comparable to that found in related bis(ligand)metal η^2-ethylene complexes of nickel and platinum (1.42–1.44 Å). This rehybridization of the olefinic C atoms toward sp^3 is also reflected in the angles observed around C6 (∠H6A–C6–H6B = 116.4 (20)°, ∠C1–C6–H6A = 117.9 (14)°, and ∠C1–C6–H6B = 116.9 (15)°).

The fulvene ring (C1–C5) is essentially planar (maximum deviation from planarity is ±0.004 Å), and the bond distances are in the typical olefinic range (C2–C3 = 1.367 (2) Å and C4–C5 1.365 (2) Å). The methyl C atoms C7–C10 are bent slightly out of the ring plane away from the metal. The deviations from planarity are as follows: C7, −0.76 (2)°; C8, −3.62 (2)°; C9, −0.57 (2)°, and C10, +0.80 (2)°. The methylenic C atom C6 suffers a similar distortion but of larger magnitude, viz., 10.81 (2)° or 0.267 (13) Å. The angle between the fulvene ring and the plane defined by Pd,P1,P2,C1,C6 is 92.2°.

Experimental Section

All operations were carried out under either pure nitrogen or argon. Toluene and pentane were dried and freed from dissolved oxygen by distillation from sodium–potassium alloy. Acetone was dried over phosphorus pentoxide. Lithium pentamethylcyclopentadienyl and ethyltetramethylcyclopentadienyl[22] and

Table IX. Analytical Data for the $[Pd(\eta^3\text{-allyl})(\eta^5\text{-}C_5Me_5)]$ and $[PdL_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ Complexes[a]

complex	mp, °C	C, %	H, %	Pd, %	P, %
3	88–92	55.18 (55.23)	7.08 (7.13)	37.71 (37.64)	
4	15–17	56.81 (56.67)	7.15 (7.47)	35.91 (35.86)	
5	63–66	56.90 (56.67)	7.19 (7.47)	35.83 (35.86)	
6	80–88	57.91 (57.98)	8.09 (7.78)	33.94 (34.24)	
7	58	60.48 (60.27)	8.17 (8.33)	30.98 (31.40)	
8	liquid	57.86 (57.98)	8.10 (7.78)	34.08 (34.24)	
14	74	48.90 (48.93)	8.20 (8.21)	26.89 (27.09)	15.70 (15.77)
15 **16**	27–30	50.08 (50.19)	8.33 (8.42)	25.98 (26.15)	15.36 (15.23)
17	50–52	55.07 (55.40)	9.37 (9.30)	22.01 (22.31)	
18	45–47	39.10 (39.32)	6.48 (6.60)	21.52 (21.77)	
19	154–156	64.96 (64.55)	9.16 (9.60)	16.35 (16.34)	9.60 (9.51)

[a] Calculated values in parentheses.

Table X. Mass Spectral Data for the $[Pd(\eta^3\text{-allyl})(\eta^5\text{-}C_5Me_5)]$ and $[PdL_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ Complexes

complex (M_r)[a]	temp, °C	MS data, *m/e* (rel intensity, assignt)
3, $C_{13}H_{20}Pd$ (282)	50	282 (20, $[M]^+$), 240 (40, $[C_{10}H_{14}Pd]^+$), 133 (100, $[C_{10}H_{13}]^+$)
4, $C_{14}H_{22}Pd$ (296)	20	296 (23, $[M]^+$), 240 (80, $[C_{10}H_{14}Pd]^+$), 225 (31, $[C_9H_{11}Pd]^+$), 211 (29, $[C_8H_9Pd]^+$), 161 (100, $[C_4H_7Pd]^+$)
5, $C_{14}H_{22}Pd$ (296)	30	296 (10, $[M]^+$), 240 (18, $[C_{10}H_{14}Pd]^+$), 135 (42, $[C_{10}H_{15}]^+$), 134 (38, $[C_{10}H_{14}]^+$), 133 (42, $[C_{10}H_{13}]^+$), 119 (100, $[C_9H_{11}]^+$)
6, $C_{15}H_{24}Pd$ (310)	50	310 (20, $[M]^+$), 242 (65, $[C_{10}H_{16}Pd]^+$), 240 (40, $[C_{10}H_{14}Pd]^+$), 135 (100, $[C_{10}H_{15}]^+$), 134 (25, $[C_{10}H_{14}]^+$)
7, $C_{17}H_{28}Pd$ (338)	25	338 (17, $[M]^+$), 240 (100, $[C_{10}H_{14}Pd]^+$), 225 (21, $[C_9H_{11}Pd]^+$)
8, $C_{15}H_{24}Pd$ (310)	40	310 (20, $[M]^+$), 254 (20, $[C_{11}H_{16}Pd]^+$), 148 (40, $[C_{11}H_{16}]^+$)
14, $C_{16}H_{32}P_2Pd$ (392), L = PMe_3	65	392 (15, $[M]^+$), 316 (21, $[M^+ - L]$), 258 (93, $[L_2Pd]^+$), 182 (100, $[LPd]^+$)
17, $C_{22}H_{44}P_2Pd$ (476), L = PEt_3	60	476 (12, $[M]^+$), 358 (19, $[M^+ - L]$), 342 (100, $[L_2Pd]^+$)
18, $C_{16}H_{32}O_6P_2Pd$ (488), L = $P(OMe)_3$	60	488 (4, $[M]^+$), 478 (31, $[L_3Pd]^+$), 354 (100, $[L_2Pd]^+$), 333 (9, $[C_{10}H_{14}P(OMe)_2Pd]^+$)

[a] Pd, M_r 106.

$[PdCl(\eta^3\text{-allyl})]_2$(allyl = C_3H_5, 1-MeC_3H_4, 2-MeC_3H_4, 1,3-$Me_2C_3H_3$, and 2-*t*-BuC_3H_4)[10] were prepared by published procedures.

The NMR spectra were measured with the following instruments: ^1H NMR, Bruker WP80 and WH400 and Varian XL100; ^{13}C NMR, Bruker WH90 and WM300; ^{31}P NMR, Bruker WP80 and WH90. ^{31}P chemical shifts are relative to external 85% H_3PO_4.

Mass spectra were recorded with Varian CH5 and CH7 instruments. Melting points, where reported, were measured in capillaries sealed under argon by using Büchi 510 and SMP 20 instruments and are uncorrected.

Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, and the A. Bernhardt, Mikroanalytisches Laboratorium, Elbach.

$[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5Me_5)]$ (3). A suspension of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (9.6 g, 26.2 mmol) in pentane (200 mL) was cooled to −60 °C, and solid LiC_5Me_5 (7.44 g, 52.4 mmol) was added, with vigorous stirring, during 1 h. The mixture was stirred for a further 18 h at −20 °C and the resulting purple solution filtered through a D4-fritte at −20 °C. The volume of solution was reduced to ca. 20 mL and cooled at −70 °C for 24 h. Purple crystals were deposited that were isolated, washed once with 50 mL of cold (−70 °C) pentane, and dried under high vacuum (10^{-3} mmHg, −20 °C); yield 11.0 g (75%).

Compounds **4**–**8** were prepared similarly. The analytical and mass spectral data have been collected together in Tables IX and X.

$[Pd(PMe_3)(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5Me_5)]$ (9). $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5Me_5)]$ (**3**) (0.165 g, 0.56 mmol) was dissolved in toluene-d_8 (1.2 mL), the mixture was cooled to −60 °C, and PMe_3 (56 μL, 0.56 mmol) was added dropwise with constant stirring. The purple solution was filtered through a D4-fritte directly into a NMR tube at −60 °C.

Compounds **10**–**13** were prepared similarly, and the NMR-data have been collected together in Tables II and IV.

$[Pd(PMe_3)_2(\eta^2\text{-}CH_2{=}C_5Me_4)$ (14). **(I)** $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5Me_5)]$ (**3**) (0.683 g, 2.3 mmol) was dissolved in pentane (20 mL), the mixture was cooled to −60 °C, and PMe_3 (0.47 mL, 4.6 mmol) was added dropwise. The purple solution was allowed to warm up to room temperature during the course of 1 h. The resulting yellow solution was filtered through a D4-fritte at room temperature and the volume reduced to ca. 5 mL. On storing at −70 °C for 24 h, yellow crystals were deposited that were collected and washed once with cold pentane (5 mL, −78 °C) and dried under high vacuum at 20 °C; yield 0.72 g (80%).

(II) A purple solution of $[Pd(PMe_3)(\eta^1\text{-}2\text{-}MeC_3H_4)(\eta^5\text{-}C_5Me_5)]$ (**10**) was kept at −20 °C for 24 h and the ^1H NMR spectrum recorded: the spectra consisted of resonances attributable to **4** (50%) and **14** (50%) as well as to isobutene [δ(Me) 1.59 (t, J = 1.5 Hz), $\delta(CH_2)$ 4.77 (sept, J = 1.5 Hz)].

Complexes **15**–**19** were prepared similarly with the exception of the $Cy_2PC_2H_4PCy_2$-stabilized complex **19** which precipitated from the pentane solution during the reaction. Analytical and mass spectral data have been collected together in Tables IX and X.

Reactions of the $[PdL_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ Complexes. (I) With Methyl Iodide. A 1.00-mmol sample of **14** was dissolved in acetone (10 mL) at room temperature. Methyl iodide (0.14 g, 1.00 mmol) was added dropwise and the solution stirred for 3 h. The volume of acetone was reduced, and diethyl ether (5 mL) was added and the solution cooled to −78 °C. After 3 days, colorless crystals of $[PdI(Me)(PMe_3)_2]$ had been deposited. These were collected, washed with pentane, and dried under high vacuum: yield 96%; mp 104 °C dec. The compound was identified by comparison of the NMR spectra with those of an authentic sample.[15] $[PdI(Me)(PEt_3)_2]$ was prepared similarly in 88% yield by reacting methyl iodide with (**17**).

(II) With Dimethyl Acetylenedicarboxylate. **14** (0.125 g, 0.319 mmol) was dissolved in toluene (1.2 mL), and dimethyl acetylenedicarboxylate (40 μL, 0.4 mmol) was added in a dropwise manner. The ^1H NMR spectrum of the reaction mixture showed the presence of tetramethylfulvene [δ 1.64 (s, Me), 1.78 (s, Me), 5.28 (s, CH_2)] and $[Pd(PMe_3)_2(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)]$ [δ 1.06 (d, $J_{P,H}$ = 9.5 Hz, PMe), 3.48 (s, OMe)].

Table XI. Crystal and Diffraction Data for $[Pd(PMe_3)_2(\eta^2\text{-}CH_2{=}C_5Me_4)]$ (14)

Crystal Parameters

formula $C_{16}H_{32}P_2Pd$
a = 12.139 (1) Å
b = 13.468 (2) Å
c = 12.294 (1) Å
β = 105.874 (8)°
V = 1933.23 Å^3
space group $P2_1/a$
M_r 392.42
d_{calcd} = 1.348 g cm^{-3}
Z = 4

Measurement of Intensity Data

radiatn: Mo Kα (μ = 10.965 cm^{-1}), no absorption correctn deemed necessary
reflctns measd: 6630 ($\pm h,k,l$) (1.00 ≤ ϑ ≤ 32.00)
independent observed reflctns: 5565 ($I \geq 2\sigma(I)$)
refined parameters: 300
temp: −173 °C
R = 0.0260, R_w = 0.0313
max res electronic density in the vicinity of the Pd atom: 0.74 e Å^{-3}

Table XII. Final Atomic Coordinates and Their Standard Deviations (×10^4)

atom	*x*	*y*	*z*
Pd	789 (1)	375 (1)	2645 (1)
P1	−1007 (1)	435 (1)	2890 (1)
P2	1495 (1)	−1205 (1)	2526 (1)
C1	2083 (1)	1433 (1)	2436 (1)
C2	3162 (1)	1205 (1)	3294 (1)
C3	3955 (1)	951 (1)	2738 (1)
C4	3428 (1)	1018 (1)	1520 (1)
C5	2312 (1)	1300 (1)	1332 (1)
C6	1112 (2)	1912 (1)	2636 (2)
C7	3298 (2)	1231 (1)	4542 (2)
C8	5158 (2)	593 (1)	3250 (2)
C9	4060 (2)	779 (2)	657 (2)
C10	1444 (2)	1476 (2)	220 (2)
C11	−1780 (2)	−696 (1)	3056 (2)
C12	−2045 (2)	1050 (2)	1730 (2)
C13	−1163 (2)	1152 (2)	4102 (2)
C14	652 (2)	−2317 (1)	2620 (2)
C15	2844 (2)	−1465 (1)	3594 (2)
C16	1915 (2)	−1446 (2)	1233 (2)
H6A	1197 (20)	2211 (17)	3408 (19)
H6B	605 (21)	2254 (18)	2005 (20)
H7A	2948 (22)	633 (19)	4800 (22)
H7B	4082 (23)	1250 (20)	4970 (22)
H7C	2874 (22)	1821 (19)	4754 (21)
H8A	5270 (21)	−102 (19)	3094 (21)
H8B	5732 (23)	955 (22)	3085 (23)
H8C	5369 (22)	652 (19)	4093 (22)
H9A	4252 (22)	96 (20)	677 (22)
H9B	3569 (23)	933 (22)	−103 (23)
H9C	4708 (24)	1175 (20)	722 (23)
H10A	876 (24)	982 (21)	41 (23)
H10B	1800 (22)	1470 (19)	−421 (22)
H10C	1163 (26)	2117 (23)	197 (27)
H11A	−1406 (20)	−1026 (18)	3724 (19)
H11B	−1840 (23)	−1127 (19)	2439 (23)
H11C	−2579 (23)	−506 (18)	3124 (23)
H12A	−1814 (20)	1735 (18)	1629 (19)
H12B	−2805 (22)	1042 (19)	1786 (21)
H12C	−2121 (22)	733 (20)	998 (22)
H13A	−1992 (20)	1244 (18)	4035 (20)
H13B	−853 (21)	1798 (19)	4112 (21)
H13C	−802 (22)	803 (20)	4780 (21)
H14A	−109 (20)	−2278 (17)	2000 (20)
H14B	475 (20)	− 2347 (17)	3326 (20)
H14C	1106 (24)	−2930 (20)	2592 (22)
H15A	3157 (20)	−2108 (18)	3457 (20)
H15B	3376 (19)	−933 (18)	3532 (19)
H15C	2724 (21)	−1434 (18)	4391 (21)
H16A	1272 (20)	−1377 (17)	608 (20)
H16B	2431 (21)	−918 (19)	1184 (21)
H16C	2248 (22)	−2124 (19)	1267 (22)

(III) With Thiophenol. **14** (0.20 g, 0.50 mmol) was dissolved in acetone (5 mL), and thiophenol (0.11 g, 1.00 mmol) was added.

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(22) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229.

(23) Davies, A. G.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 692.

The solution was concentrated, and yellow crystals of *trans*-[Pd(SPh)$_2$(PMe$_3$)$_2$] precipitated: yield 0.16 g (86%); mp 101 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.70–7.47, 7.20–6.87 (SPh), 1.77 (t, $J_{P,H}$ = 7.4, PMe); ^{31}P NMR (CDCl$_3$) δ −13.07 (s). Anal. Calcd for C$_{14}$H$_{16}$P$_2$S$_2$Pd: C, 45.33; H, 5.92. Found: C, 44.47; H, 6.44.

(IV) With [Pd(η^3-2-MeC$_3$H$_4$)(η^5-C$_5$H$_5$)]. A −40 °C solution of **17** (2.10 g, 4.40 mmol) in pentane (10 mL) was added at −40 °C to a pentane solution (10 mL) of [Pd(η^3-2-MeC$_3$H$_4$)(η^5-C$_5$H$_5$)] (1.00 g, 4.40 mmol). The solution was allowed to reach room temperature under continuous stirring. After 4 h the yellow solution was concentrated, cooled to −78 °C, and left for several days. The resulting yellow precipitate was collected, washed several times with cold pentane, and dried under high vacuum to give [Pd$_2$(PEt$_3$)$_2$(μ-2-MeC$_3$H$_4$)(μ-C$_5$H$_5$)] (**21**). yield 1.80 g (72%); mp 62 °C. Anal. Calcd for C$_{21}$H$_{42}$P$_2$Pd$_2$: C, 44.31; H, 7.44; P, 37.38. Found: C, 44.48; H, 7.99; P, 36.55.

An analagous reaction between **17** and [Pd(η^3-2-*t*-BuC$_3$H$_4$)(η^5-C$_5$H$_5$)] led to the formation of [Pd$_2$(PEt$_3$)$_2$(μ-2-*t*-BuC$_3$H$_4$) (μ-C$_5$H$_5$)] (**23**) as yellow crystals in 65% yield; mp 58 °C dec. Anal. Calcd for C$_{24}$H$_{48}$P$_2$Pd$_2$: C, 47.15; H, 7.91; P, 34.81. Found: C, 47.50; H, 8.52; P, 33.97.

[Pd$_2$(PMe$_3$)$_2$(μ-2-MeC$_3$H$_4$)(μ-C$_5$H$_5$)] (**20**) and [Pd$_2${P(OMe)$_3$}$_2$-(μ-2-MeC$_3$H$_4$)(μ-C$_5$H$_5$)] (**22**) were prepared in related reactions between **14** and **18** with [Pd(η^3-2-MeC$_3$H$_5$)(η^5-C$_5$H$_5$)] and identified by comparison of their NMR spectra with those of authentic samples. MS (**23**, C$_{24}$H$_{48}$P$_2$Pd$_2$ (611.4), 50 °C), *m/e* (rel intensity, assignt) 342 (3, L$_2$Pd$^+$), 313 (1, (Et$_2$P)LPd$^+$), 268 (69, (C$_7$H$_{13}$)(C$_5$H$_5$)Pd$^+$), 203 (100, C$_7$H$_{13}$Pd$^+$) (L = PEt$_3$).

(V) With [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$. Pentane solutions of **17** (0.48 g, 1.00 mmol) and [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ (0.20 g, 0.50 mmol) were cooled to −40 °C, mixed, and stirred at room temperature for ca. 4 h. On cooling to −78 °C, yellow crystals of [Pd$_2$(PEt$_3$)$_2$(μ-Cl)(μ-2-MeC$_3$H$_4$)] (**24**) were precipitated: yield 0.38 g (69%); mp 82 °C dec; MS (C$_{16}$H$_{37}$ClP$_2$Pd$_2$ (539.7), 100 °C), *m/e* rel intensity, assignt) 538 (6, M$^+$), 416 (5, (EtP)(Et$_2$P)(C$_4$H$_7$)Pd$_2$$^+$), 390 (3, (Et$_2$P)$_2Pd_2$$^+$), 342 (21, L$_2Pd^+$), 314 (89, (C$_4H_7$)ClLPd$^+$), 279 (27, (C$_4H_7$)LPd$^+$), 224 (100, LPd$^+$) (L = PEt$_3$). Anal. Calcd for C$_{16}H_{37}ClP_2Pd_2$: C, 35.61; H, 6.91; P, 39.43. Found: C, 36.32; H, 6.82; P, 39.03.

Crystal Structure of [Pd(PMe$_3$)$_2$(η^2-CH$_2$=C$_5$Me$_4$)] (14). Bright yellow needles were obtained by cooling a pentane solution of **14** to −78 °C. A suitable crystal was sealed in a glass capillary under argon and mounted on an Enraf-Nonius CAD-4 diffractometer and subjected to Mo Kα radiation at −173 °C. Relevant crystal data have been brought together in Table XI. The final atomic coordinates are shown in Table XII. The structure was solved by the standard Patterson (Pd, P) and Fourier (C) methods. The structure was refined by using full-matrix techniques[24] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located in a final difference Fourier synthesis and were included in the final refinement cycles,[25] and their isotropic temperature factors were refined, converging at R = 0.0260 (R_w = 0.0313) for 5565 independently observed reflections. A total of 300 parameters were included in the refinement.

Bond lengths and angles are shown in Tables VII and VIII, and the structure is shown in Figure 1. The contents of a unit cell are shown in Figure 2: as can be seen, the molecules of **14** are stacked perpendicular to the *ac* plane. There are no unusual molecular contacts.

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Registry No. **3**, 86422-37-9; **4**, 83463-65-4; **5**, 86422-38-0; **6**, 86422-39-1; **7**, 83463-66-5; **8**, 86422-40-4; **9**, 86422-41-5; **10**, 86422-42-6; **11**, 86422-43-7; **12**, 86422-44-8; **13**, 86422-45-9; **14**, 83463-67-6; **15**, 86422-46-0; **16**, 86422-47-1; **17**, 86422-48-2; **18**, 83463-68-7; **19**, 86422-49-3; **20**, 86422-52-8; **21**, 86436-12-6; **22**, 54497-81-3; **23**, 86422-51-7; **24**, 86422-53-9; [PdCl(η^3-C$_3$H$_5$)]$_2$, 12012-95-2; [PdCl(η^3-1-MeC$_3$H$_4$)]$_2$, 86422-54-0; [PdCl(η^3-1,3-Me$_2$C$_3$H$_3$)]$_2$, 67463-14-3; [PdCl(η^3-2-*t*-BuC$_3$H$_4$)]$_2$, 73769-66-1; LiC$_5$Me$_4$Et, 71237-30-4; LiC$_5$Me$_5$, 51905-34-1; PdI(Me)(PMe$_3$)$_2$, 68146-10-1; PdI(Me)(PEt$_3$)$_2$, 18974-13-5; *trans*-[Pd(SPh)$_2$(PMe$_3$)$_2$], 86422-50-6; Pd(η^3-2-MeC$_3$H$_4$)(η^5-C$_5$H$_5$), 33593-95-2; Pd(η^3-2-*t*-BuC$_3$H$_4$)(η^5-C$_5$H$_5$), 58496-57-4; [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$, 12081-18-4; methyl iodide, 74-88-4; dimethyl acetylenedicarboxylate, 762-42-5; tetramethylfulvene, 76089-59-3; thiophenol, 108-98-5.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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[24] Scattering factors used were those given in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[25] Computer programs used in this investigation have been summarized in ref 26.

[26] Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1976**, *15*, 2511.

A Seven-Platinum Cluster Containing a Trigonal-Bipyramidal Unit as the Main Framework, Pt$_7$(2,6-Me$_2$C$_6$H$_3$NC)$_{12}$[1]

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A seven-platinum cluster, **1**, Pt$_7$(2,6-Me$_2$C$_6$H$_3$NC)$_{12}$, was prepared by the reduction of dichloro(2,6-xylyl isocyanide)platinum(II) with sodium amalgam. The cluster **1** was characterized by single-crystal X-ray diffraction. Crystal data: space group $P2_1/a$, a = 28.565 (6) Å, b = 26.694 (25) Å, c = 15.278 (3) Å, β = 119.66 (2)°, V = 10123 Å^3. The molecule contains a metal atom cluster derived from a distorted trigonal-bipyramidal unit to which two extra platinum atoms have been attached in bridging positions between one equatorial and each apical Pt atom. One of the isocyanide groups coordinates in an unusual fashion: through the C=N– group to three platinum atoms by four electrons, in such a way as to form a planar cyclic CNPt$_3$ unit.

Metal clusters are of interest as a potential bridge between homogeneous and heterogeneous catalytic reactions.[2] Many carbonyl clusters are prepared and characterized by spectroscopic and X-ray crystallographic analyses.[3]