signments are possible but only this assignment gives values for $J(AB)$ and $J(AB')$ in close agreement with those found for **10**.

Conductivity measurements on complexes **7**–**12** demonstrated a marked solvent dependence. In dichloromethane, for example, only **8** and **10** approached the value anticipated for a 1:1 electrolyte; all others showed evidence of strong association in solution, especially **11** and **12**. In either acetone or nitromethane, however, all appeared to behave as either 1:1 or 3:1 electrolytes, as formulated.

Ligands of the type CNRR′, when monodentate, are commonly viewed as aminocarbyne ligands, in which free rotation around the C–N bond is restricted through a degree of multiple C,N bonding. In keeping with this more or less established convention, it is convenient to regard the μ-CNRR′ moieties in complexes **7**–**12** as bridging carbyne ligands that contribute three electrons to the cluster as a whole. It should not be overlooked, however, that an alternative way of regarding these complexes is as dimetalated iminium salts, in which the $[\mu\text{-CNRR}']^+$ fragment functions as a two-electron donor to the cluster. In view of the physical and structural properties exhibited by similar complexes such as **1**, **2**, and $Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$,[8] this may well be the more appropriate convention to use.

The platinum(I) isocyanide dimers **3**, **4**, and **5** isolated in this study are of interest for a number of reasons. Of most interest to us is their reactivity toward electrophiles and nucleophiles, which should furnish information concerning the nature of the HOMOs and LUMOs in these complexes. We are continuing our research into the chemistry of complexes **3**–**5** which will be reported in subsequent publications.

Acknowledgment. We acknowledge the Natural Sciences and Engineering Research Council of Canada for financial support, a Summer Research Fellowship (K. N.R.), and funds to purchase the PE 283 B. We also wish to thank Dr. J. Walters of the N.R.C. Atlantic Regional Laboratory for obtaining ^{31}P NMR spectra and Johnson Matthey Ltd. for a generous loan of K_2PtCl_4.

Registry No. **1**, 87101-07-3; **2**, 87101-18-6; **3**, 87101-09-5; **4**, 87101-11-9; **5**, 87101-13-1; **6**, 87101-15-3; **7**, 87101-16-4; **8**, 87101-17-5; **9**, 87101-19-7; **10**, 87114-15-6; **11**, 87114-16-7; **12**, 87101-21-1; $Pt_2Cl_2(\mu\text{-dppm})_2$, 61250-65-5; $Pt_2I_2(\mu\text{-dppm})_2$, 61289-07-4.

Direct Synthesis of Pentaphenylcyclopentadienyl Complexes of Palladium

John Powell* and Norman I. Dowling

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received June 23, 1983

A series of pentaphenylcyclopentadienyl complexes of palladium(II) of the type $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-all})Pd$ (all = allyl, 2-chloroallyl, 2-methylallyl, 1-methylallyl, 1,1-dimethylallyl, 1-carbomethoxyallyl) have been prepared in high yield from the reaction of NaC_5Ph_5 with $[(\eta^3\text{-all})PdCl]_2$ in THF. Reaction of $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-all})Pd$ with phosphorus donor ligands results in the formation of zerovalent palladium complexes and coupled organic products. Reaction of $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-2-chloroallyl})Pd$ with PR_3 ligands gives a series of complexes $(\eta^5\text{-}C_5Ph_5)PdCl(PR_3)$ that are not synthetically accessible from the reaction of NaC_5Ph_5 with $[PdCl_2(PR_3)]_2$. Pyrolysis of $(\eta^5\text{-}C_5Ph_5)(2\text{-chloroallyl})Pd$ gives allene and the chloro-bridged dimer $[(\eta^5\text{-}C_5Ph_5)PdCl]_2$. Reduction of this dimer by activated zinc dust in the presence of $RC{\equiv}CR'$ or CO gives the palladium(I) dimers $(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}RC{\equiv}CR')Pd_2$ and $(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}CO)_2Pd_2$, respectively.

Introduction

The ability of the pentamethylcyclopentadienyl ligand to enhance the stability and solubilities of various transition-metal complexes relative to their unsubstituted cyclopentadienyl analogues has been extensively utilized in recent years.[1-5] In contrast only a few complexes of the corresponding pentaphenylcyclopentadienyl ligand have been reported. These include the complex $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$ from the reaction of $Fe(CO)_5$ and C_5Ph_5Br,[6] $(\eta^5\text{-}C_5Ph_5)_2Ni$ from the reaction of the pentaphenylcyclopentadienyl radical (C_5Ph_5) with $Ni(COD)_2$,[7] $(\eta^5\text{-}Ph_5C_5)_2Mo$ (in low yield) from $PhC{\equiv}CPh$ and $Mo(CO)_6$ heated under pressure,[8] and the palladium(I) dimer $(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_5)_2Pd_2$ obtained from the reaction of $PhC{\equiv}CPh$ with palladium acetate in methanol.[9] Recent studies of $(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_5)_2Pd_2$ have shown that $\eta^5\text{-}C_5Ph_5$ complexes may frequently be markedly more stable than their $\eta^5\text{-}C_5H_5$ analogues and that the $\eta^5\text{-}C_5Ph_5$ ligand is capable of "stabilizing" various "unusual" oxidation states.[9,10] However, an obvious difficulty impeding the development of transition-metal pentaphenylcyclopentadienyl chemistry is the lack of useful synthetic routes. In particular the steric bulk of the $C_5Ph_5^-$ anion effectively reduces its nucleophilicity with respect to ligand (e.g., chloride) substitution at metal complexes, and consequently many synthetic pathways available in cyclopentadienyl chemistry fail to give complexes when using $C_5Ph_5^-$. To date no pentaphenylcyclopentadienyl transition-metal complex has been prepared directly from the $C_5Ph_5^-$ anion. This paper reports a direct entry into pentaphenylcyclopentadienyl complexes of palladium(II) and palladium(I) starting from (pentaphenylcyclopentadienyl)sodium.

---

(1) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301.

(2) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(3) John, J.; Tsutsin, M. *Inorg. Chem.* **1981**, *20*, 1002.

(4) Marks, T. J.; Manoiguez, J. M.; Fagan, P. J.; Day, W. V.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 3*, 131.

(5) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190.

(6) McVey, S.; Pauson, P. L. *J. Chem. Soc.* **1965**, 4312.

(7) Schott, A.; Schott, H.; Wilke, G.; Brandt, J.; Hoberg, H.; Hoffmann, E. G. *Liebigs. Ann. Chem.* **1973**, 508.

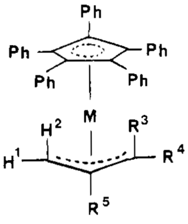
(8) Hubel, W.; Merenyi, R. *J. Organomet. Chem.* **1964**, *2*, 213.

(9) Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707.

(10) Broadley, K.; Lane, G. A.; Connelly, N. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 2486.

0276-7333/83/2302-1742$01.50/0

Table I. ^1H NMR Data for (η^5-Pentaphenylcyclopentadienyl)(η^3-allylic)palladium(II) Complexes (60 MHz, $CDCl_3$, 34 °C)



1-7

1, $R_3 = R_4 = R_5 = H$, M = Pd
2, $R_3 = R_5 = H$, R_4 = Me, M = Pd
3, $R_5 = H$, $R_3 = R_4$ = Me, M = Pd
4, $R_3 = R_4 = H$, R_5 = Me, M = Pd
5, $R_3 = R_4 = H$, R_5 = Cl, M = Pd
6, $R_3 = R_5 = H$, $R_4 = COOCH_3$, M = Pd
7, $R_3 = R_4 = R_5 = H$, M = Pt

	δ (multiplicity,[a] J (Hz))					
complex	H_1	H_2	H_3	H_4	H_5	Ph
1	2.66 (d, $J_{1-5} = 11$)	3.65 (d, $J_{2-5} = 7$)			5.3 (m)	7.03 (s)
2	2.54 (d, $J_{1-5} = 11$)	3.49 (d, $J_{2-5} = 6$)	3.34 (m, $J_{3-4} = 6$)	1.35 (d)	5.1 (m)	6.94 (s)
3	2.92 (d, $J_{1-5} = 11$)	3.50 (d, $J_{2-5} = 7$)	1.17 (s)	1.49 (s)	5.03 (dd)	7.00 (s)
4	2.59 (s)	3.47 (s)			2.06 (s)	7.05 (s)
5	2.93 (d, $J_{1-2} = 1$)	3.83 (d)				7.05 (s)
6	2.96 (d, $J_{1-5} = 12$)	3.64 (d, $J_{2-5} = 7.5$)	3.40 (d, $J_{3-5} = 10$)	3.42 (s)	6.1 (m)	7.01 (s)
7	2.33 (d, $J_{1-5} = 8.9$, $J_{Pt-H_1} = 55.4$)	3.58 (d, $J_{2-5} = 5.3$, $J_{Pt-H_2} = 29.3$)			4.3 (m)	7.04 (s)

[a] Notation: s, singlet; d, doublet; m, multiplet.

Results and Discussion

(η^5-Pentaphenylcyclopentadienyl)(η^3-allylic)palladium(II) Complexes. The complexes (η^5-C_5Ph_5)(η^3-all)Pd^{II} (η^3-all = allyl, 1-methylallyl, 1,1-dimethylallyl, 2-methylallyl, 2-chloroallyl) (**1**–**5**) were readily prepared (ca. 80% yields) by the reaction of sodium pentaphenylcyclopentadienide[11] with the appropriate chloride-bridged (η^3-allylic)palladium(II) complexes in dried THF, in an analogous fashion to the reported synthesis of (η^5-C_5H_5)(η^3-C_3H_5)Pd^{II}.[12] The complexes were isolated as red-purple crystalline materials on recrystallization from dichloromethane–methanol and were characterized by elemental analyses and ^1H NMR spectroscopy (see Table I). The attempted reaction of (1-carbomethoxyallyl)palladium chloride dimer with sodium pentaphenylcyclopentadienide under identical conditions gave initially a green solution of the expected complex (η^5-pentaphenylcyclopentadienyl)(η^3-1-carbomethoxyallyl)palladium(II), **6**, which could be isolated as a green solid on rapid workup. However, on prolonged reaction time the complex (η^5-C_5Ph_5)(η^3-1-$CO_2MeC_3H_4$)Pd^{II} decomposed to elemental palladium and the coupled organic product *trans*-$C_5Ph_5CH_2CH{=}CHCOOMe$.

Reaction of sodium pentaphenylcyclopentadienide with tetrameric (η^3-allyl)platinum chloride gave, after 10 h, a 20% yield of the complex (η^5-C_5Ph_5)(η^3-C_3H_5)Pt^{II}, **7**, isolated as an orange solid. The ^1H NMR data (Table I) for complexes **1**–**7** are fully consistent with previous NMR studies of their unsubstituted (η^5-C_5H_5)(all)Pd^{II} analogues. Platinum–hydrogen spin–spin couplings of 55.4 Hz, Pt–H(anti), and 29.3 Hz, Pt–H(syn), for complex **7** are in excellent agreement with values of 54 Hz, Pt–H(anti), and 29 Hz, Pt–H(syn), reported for the complex (η^5-C_5H_5)(η^3-C_3H_5)Pt^{II}.[13] A comparison of the chemical shifts of the allylic protons for the complexes (all = allyl, 2-methylallyl, and 2-chloroallyl (**1**, **4**, and **5**)) with the corresponding unsubstituted cyclopentadienyl derivatives shows a *deshielding* effect of the order of 0.3–0.4 ppm for the anti-allylic protons in all cases while the syn-allylic protons show a smaller net *shielding* effect. The nonequivalent and opposite shifts for a given syn–anti pair of protons are best seen as an effect of the differing degree to which these protons are affected by the chemical anisotropy of the proximate phenyl groups of the η^5-C_5Ph_5 ligand. For complex **1** the central allylic proton is deshielded by 0.33 ppm, whereas the methyl group in the (η^3-2-methylallyl) complex **4** shows a downfield shift of approximately one-third this value. These shifts are of a comparable order, as a time averaging of the anisotropic downfield shift over the three protons of the methyl group is expected. The appearance of the phenyl resonances in the spectra of all the complexes as a sharp singlet is indicative of a freely rotating η^5-C_5Ph_5 ring, paralleling the behavior of the analogous unsubstituted (η^5-C_5H_5)(η^3-allylic)Pd^{II} complexes.[3,14]

The 70-eV electron-impact mass spectra of the series of complexes **1**–**7** were obtained as part of the normal characterization procedure for these complexes. The ions of *m/e* values greater than 446 (due to the $C_5Ph_5H^+$ ion) observed in the mass spectra of complexes **1**–**7** are presented in Table II. All complexes exhibited a fragment ion, derived from coupling of the pentaphenylcyclopentadienyl ring with the allylic ligand. The generation of this ion through loss of the central metal atom probably arises as a result of thermal decomposition of the complex in the probe of the mass spectrometer. Parent molecular ions were observed for **3**, **4**, and **7** and each displayed a different fragmentation mode for loss of the allylic unit in the primary fragmentation step (see Scheme I). The molecular ion derived from the complex (η^5-C_5Ph_5)(η^3-2-MeC_3H_4)Pd^{II}, **4**, underwent simple allylic cleavage with formation of the primary fragment ion $PdC_5Ph_5^+$. For the complex (η^5-C_5Ph_5)(η^3-1,1-$Me_2C_3H_3$)Pd^{II}, **3**, the preferred mode of fragmentation of the parent molecular ion involves hydrogen transfer *from* the allylic ligand with expulsion of the neutral isoprene unit and committant formation of

---

[11] Zhang, R.; Tsutsin, M.; Bergbreiter, D. E. *J. Organomet. Chem.* **1982**, *229*, 109.

[12] Shaw, B. L. *Proc. Chem. Soc., London* **1960**, 247.

[13] Shaw, B. L.; Sheppard, N. *Chem. Ind. (London)* **1961**, 517.

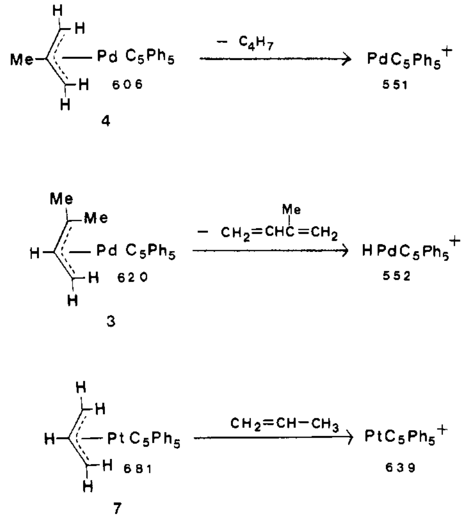
[14] Maddox, M. L.; Stafford, S. L.; Kaesz, H. D. *Adv. Organomet. Chem.* **1965**, *3*, 126.

Table II. Selected Mass Spectral Data {Ions of *m/e* Values Greater Than 446 (the $C_5Ph_5H^+$ Ion)} for the Complexes $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-all})M^{II}$ (M = Pd, Pt)[a]

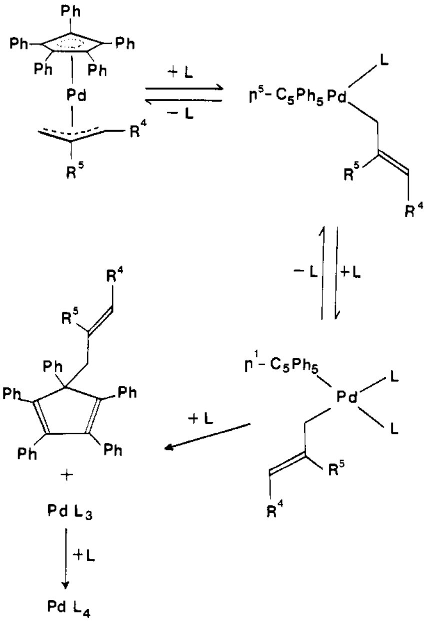
complex	allylic ligand	*m/e* [rel abundance]	ion
1	η^3-allyl	486 [170]	$C_3H_5C_5Ph_5^+$
2	η^3-1-methylallyl	500 [77]	$MeC_3H_4C_5Ph_5^+$
3	η^3-1,1-dimethylallyl	620 [0.7]	$Me_2C_3H_3PdC_5Ph_5^+$
		552 [1.2]	$HPdC_5Ph_5^+$
		514 [16]	$Me_2C_3H_3C_5Ph_5^+$
4	η^3-2-methylallyl	606 [19]	$MeC_3H_4PdC_5Ph_5^+$
		551 [3.2]	$PdC_5Ph_5^+$
		500 [16]	$MeC_3H_4C_5Ph_5^+$
5	η^3-2-chloroallyl	520 [93]	$ClC_3H_4C_5Ph_5^+$
6	η^3-1-carbomethoxyallyl	544 [109]	$COOMeC_3H_4C_5Ph_5^+$
7	η^3-allyl	681 [32.5]	$C_3H_5PtC_5Ph_5^+$
		639 [3]	$PtC_5Ph_4C_6H_4^+$
		486 [26.4]	$C_3H_5C_5Ph_5^+$

[a] Relative abundance based on $C_5Ph_5H^*$ ion = 100%.

Scheme I



Scheme II



the fragment ion $HPdC_5Ph_5^+$. This behavior parallels that for the complex $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)Pd^{II}$, the only unsubstituted cyclopentadienyl(η^3-allylic)palladium(II) complex for which mass spectral data has been reported,[15] where expulsion of the neutral allene fragment is one of the two preferred modes of fragmentation of the parent molecular ion, the other being direct cleavage of the Pd–C_5H_5 bond. The absence of a parent molecular ion in the mass spectrum of the complex $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-}C_3H_5)Pd^{II}$, 1, precludes a direct comparison in this case. In contrast, the complex $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-}C_3H_5)Pt^{II}$, 7, displayed a fragmentation involving hydrogen transfer *to* the allylic unit from the pentaphenylcyclopentadienyl ligand with expulsion of a neutral propene molecule. The origin of the transferred hydrogen atom was substantiated by the appearance of a peak at *m/e* 639 due to the fragment ion $PtC_5Ph_4C_6H_4^+$, as well as a metastable peak for this transition. The ion $PtC_5Ph_4C_6H_4^+$ further underwent secondary fragmentation, giving rise to the $C_5Ph_4C_6H_4^+$ ion, *m/e* 444. The preferential breakdown of (η^3-allyl)platinum complexes by fragmentations leading to expulsion of propene has been previously realized from a mass spectral study of the isoleptic complex $(\eta^3\text{-}C_3H_5)_2Pt$, in contrast to the palladium analogue $(\eta^3\text{-}C_3H_5)_2Pd$ which exhibited simple allylic cleavage.[16]

Reaction of $(\eta^5\text{-}C_5Ph_5)(\eta^3\text{-allylic})Pd^{II}$ Complexes with Triphenyl Phosphite. A detailed study by Werner[17] of the ligand displacement reactions of the unsubstituted complexes $(\eta^5\text{-}C_5H_5)(\eta^3\text{-all})Pd^{II}$ (all = 2-methylallyl, 1,1,2-trimethylallyl) with various Lewis bases L to form PdL_4 and the organic reaction product has shown the primary step to proceed via a $\eta^3 \rightarrow \eta^1$ rearrangement of the allylic ligand. The organic products generated in these reactions were further shown to be the 1-isomers of the corresponding allylcyclopentadienes, by rearrangement via [1,5] H shifts of the initially formed highly labile 5-isomers. We have observed similar results for the reaction of complexes 1–5 with the Lewis base triphenyl phosphite in deuteriochloroform solution (studied by proton NMR spectroscopy). The mechanistic scheme outlined in Scheme II accounts for the observed ligand displacement reactions of complexes 1, 2, and 4. Under similar conditions of concentration and temperature, the order for the ease of reaction was $(\eta^3\text{-allyl})(\eta^5\text{-}C_5Ph_5)Pd \approx (\eta^3\text{-1-methylallyl})(\eta^5\text{-}C_5Ph_5)Pd \gg (\eta^3\text{-2-methylallyl})(\eta^5\text{-}C_5Ph_5)Pd$. (For both the allyl and 1-methylallyl complexes displacement was virtually complete on addition of 2 mol equiv of triphenyl phosphite, while the 2-methylallyl complex required approximately 10 days to effect total displacement.) This order of reactivity agrees well with previous results which determined an identical sequence for the ease of formation of a η^1-allylic species from cor-

---

(15) King, R. B. *Appl. Spectrosc.* **1969**, *23*, 148.

(16) Beconsall, J. K.; Job, B. E.; and O'Brien, S. *J. Chem. Soc. A* **1967**, 423.

(17) Werner, H.; Parker, G. *Helv. Chim. Acta* **1973**, *56*, 2819.

responding (η^3-allylic)palladium precursors.[18]

Complexes **3** and **5**, on reaction with triphenyl phosphite, did not yield the coupled organic compounds as the major reaction product. Complex **3** was observed to yield isoprene and pentaphenylcyclopentatiene (eq 1). This is

$$(\eta^3\text{-}Me_2CCHCH_2)Pd(C_5Ph_5) + 4P(OPh)_3 \rightarrow H_2C{=}C(Me)CH{=}CH_2 + HC_5Ph_5 + Pd\{P(OPh)_3\}_4 \quad (1)$$

analogous to the formation of 1,3-dimethylbutadiene and cyclopentadiene from the complex (η^3-1,1,2-trimethylallyl)(η^5-C_5H_5)Pd^{II} on reaction with Lewis bases.[17] Similarly, the complex (η^3-2-chloroallyl)(η^5-C_5Ph_5)Pd^{II} on reaction with triphenyl phosphite was found to parallel the behavior of its unsubstituted analogue[19] to yield allene and the complex chloro(η^5-pentaphenylcyclopentadienyl)(triphenyl phosphite)palladium(II) (eq 2).

$$(\eta^3\text{-}2\text{-}ClC_3H_4)(\eta^5\text{-}Ph_5C_5)Pd + P(OPh)_3 \rightarrow C_3H_4 + (\eta^5\text{-}Ph_5C_5)Cl\{P(OPh)_3\}Pd \quad (2)$$

Bis(μ-Chloro)bis(pentaphenylcyclopentadienyl)dipalladium(II). Pyrolysis of (η^3-2-chloroallyl)(η^5-pentaphenylcyclopentadienyl)palladium(II), **5**, in vacuo, gave a near quantitative conversion to the brown complex bis(μ-chloro)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II), **8**, as a result of allene elimination (eq 3).

$$\underset{\mathbf{5}}{(\eta^3\text{-}2\text{-}ClC_3H_4)(\eta^5\text{-}C_5Ph_5)Pd} \xrightarrow{\Delta} C_3H_4 + \underset{\mathbf{8}}{[Cl(C_5Ph_5)Pd]_2} \quad (3)$$

Particular attention to the bath temperature, 174–176 °C (corresponds to a pyrolysis temperature of ca. 150 °C) was necessary, if thermal decomposition of **8** to a dark brown solid was to be avoided. The formation of **8** could also be achieved by refluxing a chloroform solution of complex **5** and from the reaction of $PdCl_2(PhCN)_2$ with 1 molar equiv of NaC_5Ph_5 in THF.

The ^1H NMR spectrum of complex **8** showed one broad singlet at δ 7.0 for the phenyl protons. Molecular weight studies and a broad absorption at 283 cm^{-1} in the far-infrared spectrum of **8**, assigned to the Pd-bridging chlorine stretching modes, confirm the μ-chloro dimeric structure **8**. Complex **8** represents the first truly characterized halo-bridged (η^5-cyclopentadienyl)palladium(II) complex. The value of 283 cm^{-1} for the band assigned to the ($Pd{-}Cl_b$) stretch is anywhere from 20 to 40 cm^{-1} higher than for the corresponding stretching mode in the chloro-bridged (η^3-allylic)palladium complexes.[20] This can be interpreted in terms of the η^5-C_5Ph_5 ligand being a weaker δ donor than the η^3-allylic ligand.

Previous attempts to prepare halo-bridged (η^5-cyclopentadienyl)palladium(II) complexes have not been successful. A brown solid isolated by Smidt and Jira in 1959[21] from the reaction of cyclopentadiene and aqueous palladium chloride was postulated as being the complex [(η^5-C_5H_5)$PdCl$]$_2$. However, there is some doubt as to the nature of this compound, and it has been suggested it may be a nonstoichiometric polymer. Subsequently, Robinson and Shaw[22] were unable to isolate any pure product from the reaction of cyclopentadiene and methanolic sodium chloropalladate. Reaction of a variety of 1-(1-substituted ethyl)-1,2,3,4,5-pentamethylcyclopentadienes with palladium chloride under acidic conditions results only in formation of η^4-diene complexes of the type $Pd(C_5Me_5Y)Cl_2$,[23] in contrast to similar reactions with rhodium and iridium which give chloro-bridged (η^5-C_5Me_5) complexes.[1]

Reactions of [(η^5-C_5Ph_5)$PdCl$]$_2$ with π Acids. The complex [(η^5-C_5Ph_5)$PdCl$]$_2$, **8**, was found to react reversibly with the π-acid ligands carbon monoxide, ethylene and allene, in chlorinated solvents at room temperature to form a series of kinetically labile monoadducts. When carbon monoxide is bubbled through a chloroform solution of complex **8**, the initial dark orange coloration of the dimer is lost and the solution becomes green. The infrared spectrum of the dichloromethane solution showed only one band in the 2300–1650 cm^{-1} range at 2090 cm^{-1}, assigned to the terminal carbonyl ν(CO) stretch of the complex (η^5-C_5Ph_5)$PdCl(CO)$, **9**. The value for the ν(CO) stretch of 2090 cm^{-1} found for complex **9** lies between those values determined for well-defined cationic and anionic complexes,[24-26] as would be expected for a neutral species. On purging the solution with nitrogen or direct removal of solvent, the only species isolated was the starting complex **8**. Bubbling ethylene through a deuteriochloroform solution of complex **8** again caused a change in color from dark orange to green consistent with the formation of (η^5-C_5Ph_5)$Pd(C_2H_4)Cl$, **10**. The ^1H NMR spectrum exhibited a broad singlet at δ 7.05 for the phenyl protons of the η^5-C_5Ph_5 ligand together with a sharp singlet at δ 4.53 (coordinated C_2H_4) and a further sharp singlet at δ 5.35 due to uncoordinated ethylene. The appearance of both free and coordinated ethylene resonances as sharp singlets at 34 °C indicates intermoledular exchange between free and coordinated ethylene must be slow at this temperature. The following series of equilibria therefore adequately describes the reaction between complex **8** and ethylene.

$$[C_5Ph_5PdCl]_2 + 2C_2H_4 \overset{K_{eq}}{\rightleftharpoons} 2[C_5Ph_5PdCl(C_2H_4)]$$

$$[C_5Ph_5PdCl(C_2H_4)] + C_2H_4^* \overset{\text{slow}}{\rightleftharpoons} [C_5Ph_5PdCl(C_2H_4^*)] + C_2H_4$$

$$K_{eq} = \frac{[C_5Ph_5PdCl(C_2H_4)]^2}{[(C_5Ph_5)_2Pd_2Cl_2][C_2H_4]^2} = 4.7 \text{ L mol}^{-1} \ (34\ °C)$$

(Integration of the resonances for free and complexed ethylene, as well as the total phenyl region, allowed the absolute concentrations of dimer **8**, adduct **10**, and free ethylene to be determined and hence K_{eq} to be calculated.) The reaction of complex **8** with allene in deuteriochloroform solution gave a palladium(II) allene complex, [$C_5Ph_5PdCl(C_3H_4)$], **11**. Complexation of allene was supported by the green color of the solution (by analogy to the reactions of [C_5Ph_5PdCl]$_2$ with CO and ethylene) as well as by infrared and ^1H NMR spectral data. The solution infrared spectrum of complex **11** (in $CDCl_3$) showed two weak ν(C=C) bands at 1817 and 1677 cm^{-1}, indicating a close analogy to silver(I) and copper(I) allene complexes.[27] The ^1H NMR spectrum for the reaction of complex **8** with allene in deuteriochloroform showed a broad singlet at δ 7.05 due to the phenyl protons, a sharp singlet at δ 4.63 due to free allene, and two broad peaks at δ 5.69 and 3.88 assigned to the coordinated allene in **11**. No change in these peaks was observed on cooling to −60 °C. A value for the K_{eq} (see above) of 1.3 L mol^{-1} was calculated for

---

(18) Hughes, R. P.; Powell, J. *J. Am. Chem. Soc.* **1972**, *94*, 7723.
(19) Tune, D. J.; Werner, H. *Helv. Chim. Acta* **1975**, *58*, 2240.
(20) Lupin, M. S.; Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1410.
(21) Smidt, J.; Jira, R. *Angew. Chem.* **1959**, *71*, 651.
(22) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1964**, 5002.
(23) Balakrishnan, P. V.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 1721.
(24) Majina, T.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *134*, C45.
(25) Clark, H. C.; Dixon, K. R.; Jacobs, J. W. *Chem. Commun.* **1968**, 93.
(26) Kingston, J. V.; Scollary, G. R. *Chem. Commun.* **1970**, 362.
(27) Nagendrappa, G.; Joshi, G. C.; Devaprabhakara, D. *J. Organomet. Chem.* **1971**, *27*, 421.

Table III. ^{1}H NMR Data for the Complexes (η^5-C_5Ph_5)PdCl(L) (12-19) Excluding Phosphorous Donor Phenyl Resonances (60 MHz, $CDCl_3$, 34 °C)

		δ (multiplicity, *J* (Hz))		
complex	L	CH_2	CH_3	C_5Ph_5
15	PMe_3		1.42 (d, J_{PH} = 11.5)	7.06 (s)
16	PMe_2Ph		1.58 (d, J_{PH} = 10.5)	7.02 (s)
17	$PMePh_2$		1.85 (d, J_{PH} = 11)	6.97 (s)
18	$PEtPh_2$	2.59 (dq, J_{PH} = 8.5, $J_{CH_2\text{-}CH_3}$ = 7.5)	1.07 (dt, J_{PH} = 17.5)	6.97 (s)
19	PPh_3			6.98 (s)
12	$P(OMe)_3$		3.73 (d, J_{PH} = 13)	7.06 (s)
13	$P(OEt)_3$	4.2 (dq, J_{PH} = 8, $J_{CH_2\text{-}CH_3}$ = 7)	1.13 (t, J_{PH} = 0)	7.06 (s)
14	$P(OPh)_3$			7.13 (s)

[a] Notation: s, singlet, d, doublet; t, triplet; q, quartet.

Table IV. Spectroscopic Data for the Complexes [(η^5-C_5Ph_5)Pd]$_2$(acetylene) (21-25)

bridging acetylene	^{1}H NMR[a] (60 MHz, 34 °C)	UV-visible[b]/nm	crystalline appearance	mp/°C	mass spectral data,[c] major organic fragments
21 C_2H_2	δ(≡CH) 5.86 (s), 5.79 (s, CS_2)	651, <371 (sh)	dark green	167-168	$C_5Ph_5^+$ (445)
22 C_2Et_2	δ(CH_3) 1.02 (t) δ(CH_2) 2.80 (q)	678, 380	green	251-255 dec	$C_5Ph_5^+$ (445) $C_2Et_2 - H^+$ (81)
23 $C_2(C_6H_4\text{-}p\text{-}Me)_2$	δ(CH_3) 2.27 (s)	661, 394	dark olive green	267-272 dec	$C_5Ph_5^+$ (445) $C_2(C_6H_4CH_3)_2^+$ (206)
25 $C_2(COOMe)_2$	δ(OCH_3) 3.42 (s)	702, 402	green	197 dec	$C_5Ph_5^+$ (445) $C_2CO_2MeCO^+$ (111)

[a] Chemical shifts in ppm downfield from Me_4Si. Spectra run in $CDCl_3$ solution unless otherwise stated. Notation for multiplicity: s, singlet; t, triplet, q, quartet. [b] Recorded in $CHCl_3$ solution. Notation: sh, shoulder. [c] Ion assignment (*m/e*).

this reaction. Comparison with the value of 4.7 L mol^{-1} determined for the K_{eq} of the reaction of complex 8 with ethylene indicates allene to be a worse coordinating ligand than ethylene toward palladium(II) in the present system. A similar order of coordinative abilities has been established previously for the silver(I) system, where the argentation constant for allene was found to be lower than that of ethylene.[28]

Phosphine and phosphite complexes, of formula (η^5-C_5Ph_5)PdCl(P) (P = $P(OMe)_3$, **12**, $P(OEt)_3$, **13**, $P(OPh)_3$, **14**, PMe_3, **15**, PMe_2Ph, **16**, $PMePh_2$, **17**, $PEtPh_2$, **18**, and PPh_3, **19**), were preapred by mild reflux of a chloroform solution of the complex (η^3-2-chloroallyl)(η^5-C_5Ph_5)Pd^{II}, **5**, with a stoichiometric ratio of the appropriate phosphine or phosphite. Proton chemical shifts and coupling constants, as well as $^{31}P-^1H$ coupling constants for the complexes are presented in Table III. Mass peaks due to the $C_5Ph_5H^+$ ion (*m/e* 446) and to the parent ion of the phosphine or phosphite ligand appeared in the mass spectra of all the complexes. Under identical reaction conditions none of the expected product could be isolated from the reaction of **5** with tricyclohexylphosphine, and this is attributed to the large steric bulk of this phosphine. Formation of the complex **17** by direct reaction of diphenylmethylphosphine with complex **8** in chloroform was only achieved in *very low yields*. Varying the solvent to sodium-dried benzene, or THF, and also carrying out the reaction in the cold in toluene did not improve the yield of reaction. Thus, complex **8** shows a difference in reactivity to the (η^3-allylic)palladium halide complexes, which readily undergo bridge cleavage reactions with phosphines to give the asymmetrically bonded (η^3-allylic)chloropalladium phosphine adducts.

The analogous unsubstituted complexes [(η^5-C_5H_5)PdCl(P)] (P = PEt_3, X = Cl, Br, I; P = P-*i*-Pr_3, X = Br; P = PPh_3, X = Br) were first prepared by Cross and Wardle in 1971 by reaction of the binuclear halogen-bridged phosphine complexes $(R_3P)_2Pd_2X_4$ with thallium(I) cyclopentadienide in THF solution.[29] This particular synthetic route was totally unsuitable, however, for the preparation of the phosphine adducts, as evidenced by the complete failure of the reaction of bis(μ-chloro)dichlorobis(dimethylphenylphosphine)dipalladium(II) with NaC_5Ph_5 in THF solution, to form any complex **16**. Use of TlC_5Ph_5 was also unsuccessful.

Formation of Acetylene- and CO-Bridged Bis(pentaphenylcyclopentadienyl)dipalladium(I) Complexes. The complex bis(μ-chloro)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II), **8**, in the presence of the appropriate acetylene and *activated* zinc dust in THF solution, undergoes reduction to the acetylene-bridged dimeric palladium(I) complexes **20–25** in 30–75% overall yield (eq 4). The ν(CO) for the carboxyl ester groups in complex

$$[Cl(C_5Ph_5)Pd]_2 + R^1C{\equiv}CR^2 \xrightarrow{Zn} (R^1C{\equiv}CR^2)(C_5Ph_5)_2Pd \quad (4)$$

20, $R^2 = R^2 = Ph$
21, $R^1 = R^2 = H$
22, $R^1 = R^2 = Et$
23, $R^1 = R^2 = p$-tolyl
24, $R^1 = Ph, R^2 = H$
25, $R^1 = R^2 = CO_2Me$

25 appeared at 1711 cm^{-1}, consistent with bridging through the acetylenic triple bond and uncoordinated carbomethoxy groups. Spectroscopic data for the new complexes are presented in Table IV. All complexes were an intense green color in chloroform solution and exhibited the two characteristic high wavelength 650–705-nm and low wavelength 370–405-nm bands in their UV–visible spectra.[9] The 70-eV electron-impact mass spectra of the complexes, with the exception of the ethyne-bridged derivative, further showed ions arising from the bridging acetylene ligands (see Table IV). Commercial zinc dust was used as the reducing agent in all reactions following a standard acti-

---

(28) Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697.

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

vation procedure (see Experimental Section). Highest yields were obtained when using a large excess of both acetylene and activated zinc, with vigorous agitation of the reaction mixture. The reaction with diphenylacetylene was followed by monitoring the appearance of the intense 668-nm absorption in the visible spectrum of **20**, for both a 1:1 and 2:1 ratio of diphenylacetylene to dimer **8**. A plot of absorption against time showed that 70–80% of reaction had occurred in the first hour, reaction being virtually complete after 3 h. The percent conversion to complex **20** based on the starting dimer **8** after 5 h for both the 1:1 and 2:1 reactions was ca. 40% and 50% respectively, suggesting the probable removal of starting complex **8** by an irreversible side reaction at a comparable rate to formation of the desired complex **20**. This contention was supported by the reduction of the dimer **8** in the *absence* of acetylenes to give an air-sensitive purple solution species, which was unreactive to added diphenylacetylene or carbon monoxide and decomposed to elemental palladium after several hours while still under nitrogen.

Bis(μ-carbonyl)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 26. Reduction of bis(μ-chloro)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II), **8**, with activated zinc dust in the presence of carbon monoxide in THF solution occurred rapidly, to afford an intense purple solution. A moderately stable mauve solid could be isolated on immediate workup of this solution; however, prolonged bubbling of carbon monoxide resulted in decomposition to elemental palladium. The infrared spectrum (KBr pellet) of the isolated mauve solid exhibited a single band at 1872 cm^{-1} in the carbonyl region, which was assigned to the stretching vibration due to bridging carbonyl groups consistent with the structure **26**. The assignment of the ν(CO) band at 1872 cm^{-1} to bridging carbonyls is based on the value of 1836 cm^{-1} reported for the bridging carbonyl stretching frequency in the complex [(η^5-C_5H_5)Ni(CO)]$_2$.[30] The complex [(η^5-C_5H_5)Pt(CO)]$_2$ (terminal CO's) exhibits ν(CO)'s at 2020 and 1966 cm^{-1}.[31] Attempts to obtain μ-1,2-diene or μ-1,3-diene complexes structurally analogous to **20**–**26** by the zinc reduction of **8** in the presence of excess diene were unsuccessful.

Attempted Preparation of (μ-PhC≡CPh)(η^5-C_5Me_5)$_2$Pd$_2$. Pentamethylcyclopentadiene was reacted with 1 mol of *n*-butyllithium in dry THF at −78 °C. The LiC$_5$Me$_5$/THF solution was allowed to warm to room temperature and then added immediately to a solution of 1 equiv of (η^3-2-chloroallyl)palladium chloride in dry THF. Attempts were made to isolate a product presumed to be (η^5-C_5Me_5)Pd(2-ClC$_3$H$_4$) from the resulting purple solution, but only insoluble brown solids could be obtained. The ^{1}H NMR of this solid was poorly defined, showing only a broad methyl resonance and some weak resonances arising from unreacted (2-chloroallyl)palladium chloride. However, if excess diphenylacetylene and activated zinc dust were added directly to the purple solution, it slowly darkened to almost black and then became a bright blue-green, over a period of 3 h. A visible spectrum of the green solution contained an intense absorption at λ_{max} 585 nm, which was the same as the λ_{max} for (μ-MeC≡CEt)(η^5-MeEtPh$_3$C$_5$)$_2$Pd$_2$.[9] All attempts to isolate a complex from this solution proved fruitless. The solution was quite air sensitive, and decomposition occurred slowly under an N$_2$ atmosphere. When the tetrahydrofuran was stripped with a flow of nitrogen, the complex decomposed as the solvent was removed. This decomposition was thought to be due to the presence of elemental palladium and residual zinc dust so some of the solution was run down a short Florisil column under a nitrogen atmosphere. However the compound decomposed on contact with the Florisil. An attempt to precipitate the compound out of the THF solution with degassed hexanes also resulted in decomposition of the compound in solution. However from the characteristic intense absorption peak in the visible region of the spectrum, the compound is postulated to be (μ-PhC≡CPh)(η^5-C_5Me_5)$_2$Pd$_2$, **27**. The instability of the η^5-C_5Me_5 complex **27** relative to the η^5-C_5Ph_5 analogue **20** is presumed to be due to the greater electron-releasing effects of the methyl ring substituents of the former as compared to the phenyl groups in **20**.[10] Attempts to prepare η^5-C_5H_5 analogues of **20** starting from (η^5-C_5H_5)(η^3-2-ClC$_3$H$_4$)Pd were not successful.

Experimental Section

Allylic palladium chloride complexes were prepared by the method of Dent, Long, and Wilkinson.[32] 5-Chloro-1,2,3,4,5-pentaphenylcyclopentadiene was prepared by the method of Ziegler and Schnell.[33] Pentamethylcyclopentadiene was prepared by the method of Bercaw,[34] and LiMe$_5$C$_5$ was obtained by using the procedure of King.[35] Carbon monoxide, ethylene, allene, various acetylenes, and all phosphines and phosphites were commercial samples, used without further purification.

(η^5-Pentaphenylcyclopentadienyl)(η^3-allyl)palladium(II), 1. Sodium pentaphenylcyclopentadienide was prepared in situ by dropwise addition under nitrogen of 5-chloro-1,2,3,4,5-pentaphenylcyclopentadiene (1.0016 g, 0.0021 mol) in dried THF (30 mL) to sodium amalgam (0.8%) (Na, 0.448 g; Hg, 4.1 mL) in dried THF (15 mL). The supernatant was transferred under nitrogen to a solution of bis(μ-chloro)bis(η^3-allyl)dipalladium(II) (0.381 g, 0.0015 mol) in dried THF (20 mL) followed by extraction of the amalgam residue with further dried THF (2 × 20 mL), and the resultant purple solution was stirred (30 min). Solvent was removed in vacuo, the residue extracted with dichloromethane and filtered to remove sodium chloride, and the filtrate evaporated to dryness under reduced pressure. Recrystallization of the residue from dichloromethane/methanol yielded the *product* as purple plates (0.95 g, 77%), mp 162–164 °C. Anal. Calcd for $C_{38}H_{30}Pd$: C, 76.98; H, 5.06. Found: C, 76.78; H, 4.97.

Similarly prepared from the appropriate (η^3-allylic)palladium chloride were as follows: **(η^5-pentaphenylcyclopentadienyl)(η^3-1-methylallyl)palladium(II), 2**, as red microprisms (0.989 g, 80%), mp 157–158 °C (Anal. Calcd for $C_{39}H_{32}Pd$: C, 77.18; H, 5.28. Found: C, 77.49; H, 5.30); **(η^5-pentaphenylcyclopentadienyl)(η^3-1,1-dimethylallyl)palladium(II), 3**, as red plates (1.025 g, 80%), mp 189–191 °C (Anal. Calcd for $C_{40}H_{34}Pd$: C, 77.37; H, 5.48. Found: C, 77.26; H, 5.53); **(η^5-pentaphenylcyclopentadienyl)(η^3-2-methylallyl)palladium(II), 4**, as purple plates (1.036 g, 82%), mp 192–194 °C (Anal. Calcd for $C_{39}H_{32}Pd$: C, 77.18; H, 5.28. Found: C, 76.94; H, 5.09); **(η^5-pentaphenylcyclopentadienyl)(η^3-2-chloroallyl)palladium(II), 5**, as purple microprisms (1.03 g, 80%), mp 166–168 °C (Anal. Calcd for $C_{38}H_{29}ClPd$: C, 72.74; H, 4.63; Cl, 5.66. Found: C, 72.46; H, 4.75; Cl, 5.58); **(η^5-pentaphenylcyclopentadienyl)(η^3-allyl)platinum(II), 7**, as an orange solid on recrystallization from hexane (0.083 g, 20%), mp 203–205 °C, from sodium pentaphenylcyclopentadienide and (η^3-allyl)platinum chloride after 10 h at room temperature (Anal. Calcd for $C_{38}H_{30}Pt$: C, 66.95; H, 4.41. Found: C, 65.86; H, 4.31).

Bis(μ-chloro)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II), 8. Method 1. Pyrolysis of (η^5-pentaphenylcyclopentadienyl)(η^3-2-chloroallyl)palladium(II) (0.5 g) in vacuo (bath temperature 174–176 °C (0.005–0.01 mmHg)) gave the *product* as brown prisms (0.444 g, 95%), mp 161–163 °C. Anal. Calcd for $C_{70}H_{50}Cl_2Pd_2$: C, 71.56; H, 4.29; Cl, 6.04. Found: C, 71.46; H, 4.27; Cl, 5.89. **Method 2.** PdCl$_2$(PhCN)$_2$ (0.77 g) was

---

[30] Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725.

[31] Fischer, E. O.; Schuster-Woldan, H.; Bittler, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1963**, *18B*, 429.

[32] Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

[33] Ziegler, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1925**, *445*, 266.

[34] Thelkel, S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

[35] King, R. B. *J. Organomet. Chem.* **1967**, *8*, 287.

added to 1 molar equiv of NaC_5Ph_5 in THF (50 mL) and the reaction stirred for 15 min. Removal of the solvent gave a brown residue that was dissolved in CH_2Cl_2 and eluted on a short Florisil column. Recrystallization from CH_2Cl_2/pentane gave **8** in 60% yields.

(η^5-Pentaphenylcyclopentadienyl)chloropalladium(II) Trimethylphosphine, 15. Trimethylphosphine (22 μL) was added to a solution of (η^5-pentaphenylcyclopentadienyl)(η^3-2-chloroallyl)palladium(II) (0.198 g) in chloroform (5 mL) under nitrogen and the solution gently refluxed at 70 °C overnight. Solvent was removed under reduced pressure and the residue columned on Florisil eluting with benzene and then chloroform. Partial evaporation of the green chloroform eluate followed by addition of hexane induced crystallization, yielding the *product* as green prisms (0.063 g, 30%), mp 187–189 °C. Anal. Calcd for $C_{38}H_{34}ClPPd$: C, 68.79; H, 5.16; Cl, 5.34. Found: C, 68.64; H, 5.36; Cl, 5.45. Similarly prepared were complexes **12–14** and **16–19**, isolated as green prisms (yields 30–65%).

(μ-Diphenylacetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 20. Dichlorobis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (0.0478 g) was stirred vigorously in dried THF (18 mL) under N_2 with 5 g of activated zinc dust and 0.121 g of diphenylacetylene until the solution turned dark green—usually about 2–4 h. The solution was then filtered and taken to dryness. The residue was taken up in benzene and chromatographed on an alumina column, eluting with benzene. The product was recrystallized from benzene/hexanes as dark green prisms (0.340 g): 65% yield; mp 241 °C dec.

(μ-Acetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 21. Dry THF (10 mL) was cooled to −50 °C and saturated at that temperature with acetylene. A 0.210-g sample of bis(μ-chloro)di(η^5-pentaphenylcyclopentadienyl)dipalladium(II) was added to the solution along with 5 g of activated Zn and the mixture stirred at 50 °C for 1 h with acetylene bubbling through the solution. The product was worked up as for **20** to give 0.149 g of bright green crystals (74% yield); mp 166–168 °C. Anal. Calcd for $C_{72}H_{52}Pd_2$: C, 76.53; H, 4.64. Found: C, 76.39; H, 4.78.

The following complexes from (a) liquid and (b) solid acetylenes were similarly prepared by (a) injection of the acetylene and (b) addition of the solid acetylene to a solution of bis(μ-chloro)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) in dried THF (10 mL) in the presence of an excess of activated zinc. The compounds were characterized by their ^{1}H NMR and characteristic UV–visible spectra and by comparison with the previously reported analogue. **(μ-Hex-3-yne)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 22:** as greem prisms (0.061 g, 73%), mp 255 °C dec, from hex-3-yne. **(μ-Di-*p*-tolylacetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 23:** as dark olive green prisms (0.088 g, 39%), mp 272 °C dec, from di-*p*-tolylacetylene. **(μ-Phenylacetylene)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 24:** as green crystals (53% yield) from phenylacetylene. **(μ-Dimethylacetylenedicarboxylate)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 25:** as olive green crystals (35% yield) from dimethylacetylene dicarboxylate.

Bis(μ-carbonyl)bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I), 26. Carbon monoxide was bubbled through a solution of bis(μ-chloro)di(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (0.277 g) in dried THF (10 mL), in the presence of a large excess of activated zinc dust, for 5 min, and the resultant dark purple solution was filtered and solvent removed under reduced pressure by using a room temperature water bath. The residue was passed down a short Florisil column eluting with benzene, and evaporation of the filtrate to dryness afforded the *product* as a mauve solid (0.12 g, 45%), decomposition to a yellow solid on warming, mp 143–146 °C. Anal. Calcd for $C_{72}H_{50}O_2Pd_2$: C, 74.55; H, 4.36. Found: C, 73.92; H, 4.41.

(μ-Diphenylacetylene)bis(η^5-pentamethylcyclopentadienyl)dipalladium(I), 27. C_5Me_5Li (0.478 g) in 19 mL of dry THF was added to (0.738 g) bis(μ-chloro)bis(2-chloroallyl)dipalladium(II) in 14.6 mL of dry THF. After about 10 min the solution was a deep purple. A 0.365-g sample of diphenylacetylene and 2 g of activated zinc were added at this point, and the resulting mixture was stirred for 3 h. The green solution had a λ_{max} of 585 nm in the visible spectrum consistent with the formation of (μ-PhC≡CPh)($Me_5C_5)_2Pd_2$, but all attempts to isolate the product from the solution were in vain.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support.

Registry No. **1**, 87183-80-0; **2**, 87183-81-1; **3**, 87183-82-2; **4**, 87183-83-3; **5**, 87183-84-4; **6**, 87183-85-5; **7**, 87183-86-6; **8**, 63946-67-8; **9**, 87183-87-7; **10**, 87183-88-8; **11**, 87183-89-9; **12**, 87183-90-2; **13**, 87183-91-3; **14**, 87183-92-4; **15**, 87183-93-5; **16**, 63947-95-5; **17**, 87183-94-6; **18**, 87183-95-7; **19**, 87183-96-8; **20**, 39459-32-0; **21**, 87183-97-9; **22**, 87183-98-0; **23**, 87183-99-1; **24**, 87184-00-7; **25**, 87184-01-8; **26**, 87184-02-9; **27**, 87184-03-0; 5-chloro-1,2,3,4,5-pentaphenylcyclopentadiene, 5724-11-8.

Demethylation of Methylcobalamin by Platinum(IV)/Platinum(II) Couples. Formation of Methylplatinum(IV) Products

Yueh-Tai Fanchiang,*[1] Joseph J. Pignatello,* and John M. Wood

Gray Freshwater Biological Institute, The University of Minnesota, Navarre, Minnesota 55392

Received April 21, 1983

The demethylation of methylcobalamin (CH_3-B_{12}) by combinations of Pt(IV) ($PtCl_6^{2-}$, $Pt(CN)_4Cl_2^{2-}$, or $Pt(CN)_5Cl^{2-}$) and Pt(II) ($PtCl_4^{2-}$ or $Pt(CN)_4^{2-}$) requires platinum in both oxidation states. The reactions occur with 1:1 stoichiometry between Pt(IV) and CH_3-B_{12}. The sole B_{12} product is H_2O-B_{12}^+, whether or not oxygen is present. ^{195}Pt and ^{13}C NMR spectroscopy is used to show that the platinum products are CH_3Pt^{IV} and Pt^{II} complexes and that the methyl group is transferred to the platinum of the Pt(II) reactant. These CH_3Pt^{IV} products are susceptible to reaction with the nucleophiles OH^-, Cl^-, and CN^- to produce the corresponding organic products CH_3OH, CH_3Cl, and CH_3CN.

Introduction

Methylcobalamin (CH_3-B_{12}) has been shown to methylate a broad range of metal and metalloid ions in aqueous solution. Such reactions have attracted considerable attention for both mechanistic and environmental reasons.[2-4] In 1971 it was reported that platinum salts in both the II and the IV oxidation states were required for the deme-

---

[1] Present address: Department of Biochemistry, Medical School, The University of Minnesota, Minneapolis, MN 55455.

0276-7333/83/2302-1748$01.50/0 © 1983 American Chemical Society