theoretical results for a molecule with the Cr–Cr distance and axial interactions characteristic of the solid state with the experimental spectrum given by isolated gaseous molecules. As for the calculation[5] per se, it appears to have given a qualitatively erroneous description of the ground state electronic structure because correlation energies were ignored. Inclusion of those effects of configuration interaction expected to be of greatest importance gives a ground state with appreciable Cr–Cr bonding, as recently shown by M. Benard and A. Veillard, *Nouv. J. Chem.*, **1**, 97 (1977). An SCF-Xα-SW calculation by G. G. Stanley and F. A. C., *Inorg. Chem.*, in press, gives a ground state with a clear-cut quadruple bond, albeit a weaker one than that in $Mo_2(O_2CCH_3)_4$.

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Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of μ-Diphenylacetylene-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I) and Related Analogues

Thomas R. Jack, Christopher J. May, and John Powell*

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada, M5S 1A1. *Received January 3, 1977*

Abstract: The reaction of diphenylacetylene with palladium acetate in alcohols leads to the formation of μ-diphenylacetylene-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I). Similar compounds of the general form $[(\mu\text{-}RC_2R')(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2]$ are more readily prepared from the reaction of the acetylene RC_2R' with *endo*-alkoxytetraarylcyclobutenylpalladium acetate in alcohol. The formation of pentasubstituted cyclopentadienyl ligands from acetylenes is a novel reaction that involves an unusually facile cleavage of an acetylene triple bond. One-half of the acetylene cleaved is lost as the ortho ester $ArC(OR)_3$. A mechanism for this reaction is proposed. The molecules $[(\mu\text{-}RC_2R')(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2]$ undergo bridge acetylene displacement reactions, react with NO to give $[(\eta^5\text{-}Ar_3RR'C_5)PdNO]$, and react with HX (X = Cl, Br) to give $[(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2X_2]$ and $[(\eta^5\text{-}Ar_3RR'C_5)_2Pd_2HX]$. The latter compounds are tentatively formulated as bridging hydrido complexes.

Recent work by Maitlis and co-workers on the mechanism of the palladium(II) chloride induced cyclotrimerization of acetylenes to benzenes has demonstrated the intermediacy of cyclopentadienylmethyl complexes in the reaction pathway.[1,2] In several cases these complexes have been isolated and in others decomposition of these intermediates leads to the formation of benzenes and/or cyclopentadiene products. In this paper we report that under suitable conditions palladium complexes containing η^5-pentasubstituted cyclopentadienyl ligands may be isolated from the reaction of acetylenes with a variety of palladium compounds in alcoholic solutions.

Results and Discussion

(i) Synthesis and Structure of $[(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_5Pd)_2]$. The reaction of diphenylacetylene with palladium acetate in methanol at 25 °C gave a dark green crystalline diamagnetic solid **1**. Microanalysis and molecular weight data (Table I) for the recrystallized compound **1** showed it to have the stoichiometry $Pd_2C_{84}H_{60}{\cdot}S$ (where S = $CHCl_3$ or C_6H_6 depending on the solvent used for the recrystallization). Attempts to ascertain the structure of **1** by chemical means proved fruitless and finally a crystal was grown (in benzene) suitable for x-ray diffraction studies. The molecular structure of **1** as determined by Nyburg and co-workers[3] is shown in Figure 1. The molecule contains a dinuclear Pd(I) unit, bridged orthogonally by a diphenylacetylene, and two pentaphenylcyclopentadienyl ligands each of which is bound to one of the Pd(I)'s. This structure is novel in several features: it is one of the few established stable formally Pd(I) species;[4–12] it is a rare example of an acetylene bridging two palladiums; and it represents a significant addition to the number of known cyclopentadienyl–palladium complexes.[2] Despite its novelty, complex **1** completes the occurrence of this structure for the nickel triad being analogous to the complex $[(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5H_5Ni)_2]$[13] and related to the complex $[(\mu\text{-}C_5H_5C_5H_5)(\eta^5\text{-}C_5H_5Pt)_2]$.[14] The intermetallic Pd–Pd distance (2.64 Å) is significantly shorter than that found in the elemental metal (2.75 Å)[15] and is comparable to the Pd–Pd bond length reported by Allegra et al.[4] for the complexes $[(\eta^6\text{-}C_6H_6)PdAlCl_3X]_2$ (2.57 Å; X = Cl or $AlCl_4$). The bridging acetylene has a carbon–carbon distance of 1.33 Å in close agreement with that observed in the nickel analogue $[(\mu\text{-}PhC{\equiv}CPh)((\eta^5\text{-}$

Table I. Analytical and Spectroscopic Data for the Complexes $[(\eta^5\text{-}Ar_3R^1R^2C_5)_2(\mu\text{-}R^3C{\equiv}CR^4)Pd_2]$

Complex	Ring substituents			Bridging acetylene		Crystalline appearance	Mp, °C	Elemental analysis[a-e] Calcd		Found		Major UV visible Abs[n] Bands[g]			Mass spectral data, major organic fragments, ion (assignment m/e)	^{1}H NMR data,[h] ethyl and methyl protons[i]
	Ar	R^1	R^2	R^3	R^4			C	H	C	H	λ_{max}, nm	($\epsilon \times 10^{-3}$), M^{-1} cm^{-1}	λ_{max},[f] nm		
1[k]	Ph	Ph	Ph	Ph	Ph	Green prisms	240 dec	79.47 72.84	4.89 4.39	79.21 72.03	5.18[a] 4.57[b]	668	(30.2)	362	$P^+ = C_5Ph_5^+$ (445); $C_2Ph_2^+$ (178)	
11a[l]	Ph	Et	Et	Et	Et	Purple prisms	175–177	72.51	6.08	72.47	5.95	588	(28.3)	374	$P^+ = C_5Ph_3EtC_2H_4^+$ (348); $C_2Et_2^+$ (82)	δCH_2 (r) 2.46 q; CH_3 (r) 1.07 t; CH_2 (b) 2.68 q; CH_3 (b) 0.95 t
11b[m]	Ph	Ph	Me	Ph	Me	Purple prisms	133–139	75.62	4.93	74.91	5.15	618	(30.6)	376	$P^+ = C_5Ph_4CH_2^+$ (382); $PhC_2CH_2^+$ (115)	δCH_3 (r) 1.77 s; CH_3 (b) 2.63 s
11c[j]	Ph	*t*-Bu	Me	*t*-Bu	Me	Yellow green solution						600		482, 329 349		
11d[j]	Ph	Et	Me	Et	Me	Blue green solution						585		367		
11e	Ph	*p*-MeO C_6H_4	*p*-MeO C_6H_4	*p*-MeO C_6H_4	*p*-MeO C_6H_4	Green prisms	142–147					669	(28.3)	397	$P^+ = C_5Ph_3(C_6H_4OMe)_2H^+$ (506); $C_2(C_6H_4OMe)_2^+$ (238)	δOMe (r) 3.70; OMe (b) 3.75
11f	Ph	*p*-tolyl	*p*-tolyl	*p*-tolyl	*p*-tolyl	Green prisms	160–164	77.15	5.22	77.44	5.42[d]	666	(31.2)	398		δCH_3 (r) 2.12; CH_3 (b) 2.24
11g	Ph	*p*-Br C_6H_4	*p*-Br C_6H_4	*p*-Br C_6H_4	*p*-Br C_6H_4	Green prisms	199–203					676	(>25)	379	$P^+ = C_5Ph_3(C_6H_4Br)_2H^+$ (606); $C_2(C_6H_4Br)_2^+$ (338) {data for ^{81}Br}	
11h	Ph	Ph	Naphth	Ph	Naphth	Green prisms	157–161	76.78	4.52	76.40	4.70[c]	674	(20.5)	401	$P^+ = C_5Ph_4$Naphth H^+ (496); C_2PhNaphth (228)	
12a	Ph	Ph	Me	Ph	Ph	Green prisms	134–136					637	(30.2)	389		δCH_3 (r) 1.70 s
12b	Ph	Et	Et	*p*-MeO C_6H_4	*p*-MeO C_6H_4	Green glass	72–73					620	(27.5)	386		δCH_2 (r) 2.30 q; CH_3 (r) 0.97 t; OMe 2.30 s
12c	Ph	Et	Et	*p*-FC_6H_4	*p*-FC_6H_4	Green glass	75–80	68.32	5.12	68.03	4.88[c]	628	(>26)	385		δCH_2 2.33 q; CH_3 0.93 t
12d	Ph	Et	Et	*p*-tolyl	*p*-tolyl	Green glass	94–98					626	(26.6)	386		δCH_2 (r) 2.26 q; CH_3 (r) 0.93 t; CH_3 (b) 2.30 s
12e[n]	Ph	Et	Et	Ph	Ph	Green prisms	161–163	68.54	5.09	67.76	4.76[b]	630	(26.0)	385	$P^+ = C_5Ph_3EtC_2H_4^+$ (348); $C_2Ph_2^+$ (178)	δCH_2 2.27 q; CH_3 0.88 t
						Green glass	81–87	75.28	5.11	75.43	5.21					
12f	Ph	Et	Et	*p*-Cl C_6H_4	*p*-Cl C_6H_4	Green prisms	90–94	70.35	5.21	70.14	5.15	636	(26.8)	390		δCH_2 2.29 q; CH_3 0.95 t
12g	Ph	Et	Et	*p*-Br C_6H_4	*p*-Br C_6H_4	Green glass	99–104					637	(28.6)	392		δCH_2 2.30 q; CH_3 0.97 t
12h	Ph	Et	Et	*p*-NO_2 C_6H_4	*p*-NO_2 C_6H_4	Green glass	108–110					673	(>26.0)	428		δCH_2 2.33 q; CH_3 1.00 t
12i	Ph	Et	Et	Ph	Me	Blue green glass	52–58	73.61	5.69	73.47	5.77	612	(>26.0)	374		δCH_2 2.30; CH_3 0.98 t; Me 2.56

13a	*p*-tolyl	*p*-tolyl	*p*-tolyl	*p*-tolyl	*p*-tolyl	Green prisms	220 dec	79.83	6.31	74.81	6.31[e]	672	(32.5)	396	δCH_3 (r) 2.15; CH_3 (b) 2.30
13b	*p*-tolyl	*p*-MeO C_6H_4	*p*-MeO C_6H_4	*p*-MeO C_6H_4	*p*-MeO C_6H_4	Green prisms	150–153					674	(>26.0)	400	δCH_3 (r) 2.32; OMe (r) 3.58; OMe (b) 3.73

[a-e] For economic reasons elemental analyses were carried out on a representative range of compounds only. Other compounds were characterized as being structurally analogous by their spectroscopic properties. The complexes in crystalline form frequently contained solvent of crystallization: [a] $1C_6H_6$; [b] $1CHCl_3$; [c] $1CH_2Cl_2$; [d] $\frac{1}{2}CH_2Cl_2$; [e] $1C_6H_{12}$. [f] Absorption appears as a shoulder on charge transfer bands, $\epsilon \times 10^{-3}$ ca. 15–26. [g] Recorded in $CHCl_3$. [h] Recorded in $CHCl_3$-*d*. [i] Ring substituents (r), bridge substituents (b). [j] Complexes prepared in solution by reaction 5, but not isolated. The complex 11c decomposes in ~30 min at 30 °C to give a yellow solution with no absorption in the region of 600 nm. [k-n] Molecular weights (g/mol) were determined osmometrically in $CHCl_3$, 37 °C: [k] calcd 1281, found 1253; [l] calcd 994, found 916; [m] calcd 1095, found 995; [n] calcd 1090, found 1082.

Table II. Analytical and Spectroscopic Data for the Pentasubstituted Cyclopentadienyl Palladium Nitrosyl and Palladium(II) Derivatives

Complex		Crystalline appearance	Mp, °C	Elemental analysis[a]						Mol wt,[d] g/mol		Major UV-visible absorption bands		Mass spectral data,[e] major organic fragments, ion (assignment *m/e*)	^1H NMR and IR Data[f]
				Calcd			Found								
No.	Formula			C	H	Cl or Br	C	H	Cl or Br	Calcd	Found	λ_{max}, nm	($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})		
14a	$(C_4Ph_4OMe)Pd\{C_5Ph_3(CO_2Me)_2\}$	Red prisms	177–178	74.46	4.91		74.37	4.99		903	937	417	(11.2)	$P^+ = C_5Ph_3(CO_2Me)_2H^+$ (410); $C_4Ph_4OCH_2^+$ (386)	δCO_2Me 3.43 (s); OMe 3.34 s
14b	$(C_4Ph_4OEt)Pd\{C_5Ph_3(CO_2Me)_2\}$	Red prisms	178–180	74.63	5.05		74.74	5.08		917	884	419	(10.9)	$P^+ = C_5Ph_3(CO_2Me)_2H^+$ (410); $C_4Ph_4OC_2H_4^+$ (400)	δCO_2Me 3.40 (s); OEt 4.72 q; 1.07 t
15a	$(C_5Ph_5)PdNO$	Purple prisms[b]	151–154	68.40	4.20		68.90	4.37[b]				539	(3.3)	$P^+ = C_5Ph_5H^+$ (446); "no peaks at 178 $(C_2Ph_2^+)$"	ν_{NO} 1775 cm^{-1}
15b	$(C_5\text{-}p\text{-}tolyl_5)PdNO$	Purple solid										543	(3.0)	$P^+ = C_5\text{-}p\text{-}tolyl_5H^+$ (516)	ν_{NO} 1756 cm^{-1}
15c	$(C_5Ph_3Et_2)PdNO$	Purple glass	55–60	66.74	5.19		66.59	5.20				523	(3.1)	$P^+ = C_5Ph_3EtC_2H_4^+$ (348); no peaks at 82 $(C_6H_{10}^+)$	ν_{NO} 1755 cm^{-1}
16a	$(C_5Ph_5)_2Pd_2HCl$	Purple solid	167–170	73.72	4.51	3.11	73.87	4.67	4.15	1139	1210	560	(7.1)	$P^+ = C_5Ph_5H^+$ (446); no peaks at 178 $(C_2Ph_2^+)$	δCH_3 1.20 t; δCH_2 2.54 q
16b	$(C_5Ph_5)_2Pd_2HBr$	Blue-purple solid	170–173	70.94	4.30	6.75	70.86	4.34	6.68			532	(4.4)	$P^+ = C_5Ph_5H^+$ (446); no peaks at 178 $(C_2Ph_2^+)$	
16c	$(C_5\text{-}p\text{-}tolyl_5)_2Pd_2HCl$	Purple solid	134–138									570	(9.6)		δCH_3 2.10 s
17a	$(C_5Ph_5)_2Pd_2Cl_2$	Brown prisms	162–163	71.56	4.29	6.04	71.44	4.32	5.88						
17b	$(C_5Ph_5)_2Pd_2Br_2$	Orange-brown solid prisms[c]	137–140	69.34	4.40	11.25	70.33	4.38	10.91[c]						
17c	$(C_5\text{-}p\text{-}tolyl_5)_2Pd_2Cl_2$	Brown solid	160–170												δMe 2.18 s
18	$(C_5Ph_5)Pdhfac$	Brown glass[a]	68–72	58.35	3.34		58.80	3.45[a]						$P^+ = C_5Ph_5Pdhfac^+$ (748)[e]	δhfac→CH 5.85 s
19	$(C_5Ph_5)Pd(PMe_2Ph)Cl$	Pale green prisms	181–187	71.18	5.00	4.89	70.98	5.19	4.89			674		$P^+ = C_5Ph_5H^+$ (446); PMe_2Ph^+ (138)	δMe 1.62 d, J_{PH} = 10.6 Hz

[a-c] Compounds contain solvent of crystallization: [a] CH_2Cl_2; [b] $\frac{1}{2}CH_2Cl_2$; [c] $2C_6H_6$. [d] Molecular weights recorded osmometrically in $CHCl_3$ at 37 °C. [e] Mass of Pd containing species based on ^{106}Pd. [f] ^1H NMR data recorded in $CDCl_3$ solution at 37 °C. Aromatic resonances not included. s = singlet, d = 1:1 doublet, t = 1:2:1 triplet, q = 1:3:3:1 quartet. IR data recorded as Nujol mulls.

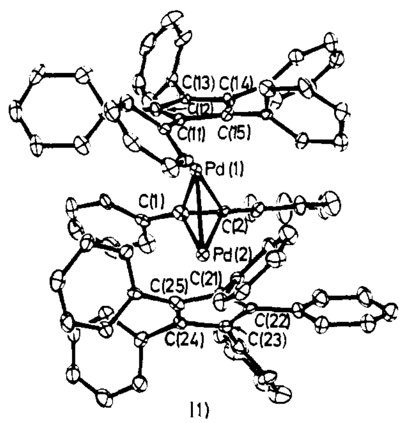


Figure 1. Molecular structure of **1** as determined by x-ray crystallography.[3]

$C_5H_5)Ni)_2]$,[13] 1.35 Å. The palladium-cyclopentadienyl carbon distance varies from 2.27 to 2.46 Å, which in light of the steric hindrance involved in the packing of the phenyl substituents in compound **1** is comparable to the Pd-C_5 distance in $[(\eta^3\text{-allyl})(\eta^5\text{-}C_5H_5)Pd]$ of 2.24 Å.[16]

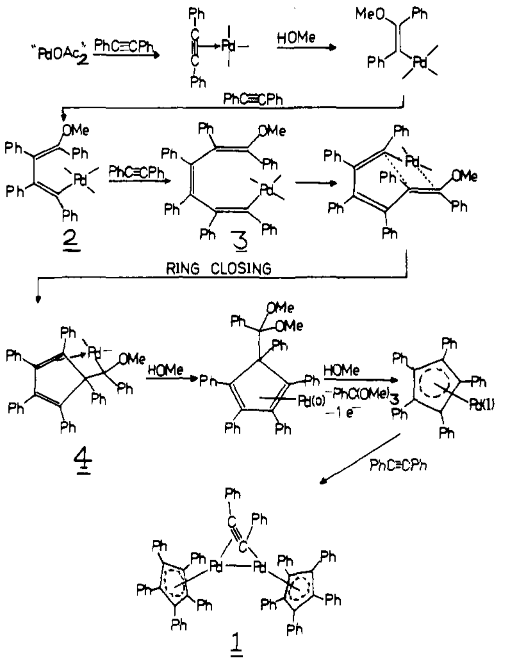
The compound **1** can also be obtained from the reaction of diphenylactylene with either $Pd(NO_3)_2{\cdot}xH_2O$, $Pd(O_2CCF_3)_2$, or $Pd(O_2CCF_3)_2(\text{acetone})_2$. Ethanol may be used in place of methanol as the solvent. The best yields of **1** are obtained with palladium acetate and diphenylacetylene in MeOH. The yields for this reaction range from 44 to 55% incorporation of the reagent palladium into the product. Of course, palladium acetate itself decomposes to elemental palladium in alcohol at a competitive rate.[17] The formation of **1** from PhC≡CPh is most unusual in that a $C_5Ph_5^-$ ring has been built up from PhC≡CPh units. This requires the facile cleavage of a carbon-carbon triple bond in a room temperature reaction. Very few instances of such a cleavage are known.[18] The formation of a cyclopentadienyl ring from acetylenes also has limited precedents, all of which occur under severe reaction conditions.[19] The nature of the reaction is therefore of considerable interest.

Analysis of the filtrate, after removal of **1**, by NMR and mass spectroscopy identified trimethoxy orthobenzoate, $PhC(OMe)_3$, as the major organic product together with a small amount of methyl benzoate. Under anhydrous conditions (MeOH distilled off $Mg(OMe)_2$) the reaction gave $PhC(OMe)_3$ as the sole organic product, which suggests that the methyl benzoate is formed by hydrolysis of the initially formed $PhC(OMe)_3$. A quantitative analysis of product yields showed that 2 mol of $PhC(OMe)_3$ were formed per mole of **1** (i.e., one $PhC(OMe)_3$ per C_5Ph_5 ring). It is of note that neither the acetal, $PhCH(OMe)_2$, nor hexaphenylbenzene was found among the reaction products. The absence of these compounds is important, since an acetal is the product of ring contraction of hexamethyl-Dewar benzene by K_2PtCl_4 in acidic media containing $SnCl_2$ to give the $(\eta^4\text{-pentamethylcyclopentadiene})PtCl_2$ species.[20,21] Hexaphenylbenzene, C_6Ph_6, is a product found in PhC≡CPh/Pd(II) halide systems.

Since palladium acetate itself decomposes in alcohol to elemental palladium, no meaningful quantitative measurement of palladium as a reaction product could be attempted. However, based on the other reagents and products, the following stoichiometry has been adopted for the formation of **1** from $Pd(OAc)_2$/PhC≡CPh in MeOH:

$$[Pd(OAc)_2]_3 + 7PhC{\equiv}CPh \xrightarrow{6MeOH} \mathbf{1}\downarrow + Pd(0)\downarrow + 2PhC(OMe)_3 + 6HOAc \quad (1)$$

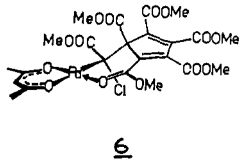
Scheme I. Mechanism Proposed for the Formation of **1** from the Reaction of Diphenylacetylene with Palladium Acetate in Methanol



Based on eq 1 yields of **1** were usually in the range of 70–85%.

(ii) **The Mechanism of the Formation of μ-Diphenylacetylene-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I).** A plausible mechanism for the formation of **1** via eq 1 is shown in Scheme I. The reaction path, as postulated, proceeds by the coordination of diphenylacetylene to Pd(II) via a π bond followed by a nucleophilic attack of an alkoxy group on the coordinated acetylene to give a σ-vinylic species. (This nucleophilic attack has been shown as trans in Scheme I on the basis of x-ray crystallographic data[22]). Further insertion of two diphenylacetylene molecules followed by rearrangement of the conformation of the triene chain yields the postulated species **3**. This can then ring close to a pentaphenylcyclopentadiene intermediate **4**.

Support for the pentaphenylcyclopentadiene species **4** can be obtained from Maitlis's work, since the reaction sequence to this point in Scheme I is as proposed by Maitlis for the formation of hexaphenylbenzene, C_6Ph_6, from diphenylacetylene and "$Pd^{II}Cl_2$" in organic solvents.[1,2] In Maitlis's system, the nucleophile is the chloride ion (rather than MeO) and the postulated pentaphenylcyclopentadiene intermediate **5** (see Scheme II) (the analogue of **4** in Scheme I) undergoes a ring expansion reaction with the subsequent dissociation of the C_6Ph_6 molecule (Scheme II). The postulated structures of the pentasubstituted cyclopentadiene species **4** (Scheme I) and **5** (Scheme II) are supported by two structurally well-defined analogues **6** and **7** reported by Maitlis and prepared from the oligomerization of the acetylenes, RC≡CR (R = Me, COOMe), by Pd(II) complexes.[23,24] The proposed pentaphenylcyclopentadiene species **4** (Scheme I) yields the dinuclear green compound **1** by the reduction of palladium and formation of $PhC(OMe)_3$. The exact mechanism of this redox



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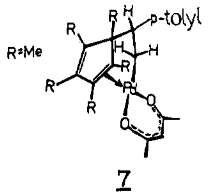

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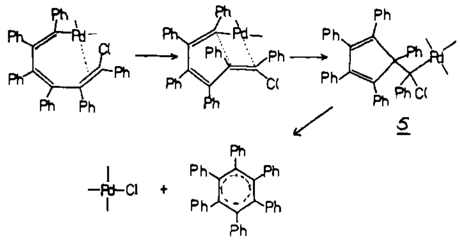
Scheme II. Intermediates in the Formation of Hexaphenylbenzene from the Reaction of Diphenylacetylene with "Palladium Chloride" According to Maitlis[1,2]



reaction is unknown, but a plausible route is shown in Scheme I.

In 1960, Malatesta et al.[25,26] reported that the reaction of diphenylacetylene and "$Pd^{II}Cl_2$" in alcohol precipitates the complex $[(endo\text{-}\eta^3\text{-alkoxytetraphenylcyclobutenyl})PdCl]_2$ (**8**) as a yellow solid for which the mechanism shown in Scheme III has since been proposed. The trans attack of methoxy in Scheme III leads to a postulated σ-butadienyl species **9** {the analogue of **2** in Scheme I} which can stereospecifically ring close to the *endo*-alkoxycyclobutenyl isomer **8** (OR = OMe) by a Woodward-Hoffmann allowed process.[1,2] Presumably it is the presence of the chloride ligand that promotes the precipitation of the product **8**, $[(endo\text{-}\eta^3\text{-alkoxytetraphenylcyclobutenyl})PdCl]_2$, in this system since in its absence, an intermediate of the type **2** has been postulated to lead to the formation of $[(\mu\text{-PhC}{\equiv}\text{CPh})(\eta^5\text{-}C_5Ph_5Pd)_2]$ **1**, see Scheme I. In the light of such a hypothesis, removal of the chloride ligand from **8** in an alcoholic solution of diphenylacetylene may lead to the formation of the green compound **1** by a *ring opening* of the *endo*-η^3-alkoxytetraphenylcyclobutenyl ring to regenerate the intermediate **2** in the mechanism Scheme I; i.e., this ring opening, if operative, would literally "plug in" to Scheme I for the formation of **1** at the proposed intermediate **2**.

(iii) **Formation and Reactivity of "*endo*-$C_4Ph_4ORPdOAc$".** It has been previously established that $[(endo\text{-}C_4Ph_4OR)PdCl]_2$ (**8**) will not react with diphenylacetylene to give C_6Ph_6.[27] Indeed a mixture of $[(endo\text{-}C_4Ph_4OR)PdCl]_2$ and PhC≡CPh in $CDCl_3$ remains unreacted after 3 days. However, in the presence of excess sodium acetate in warm MeOH, the mixture of PhC≡CPh and $[(endo\text{-}C_4Ph_4OMe)PdCl]_2$ quickly assumes the green color characteristic of $[(\mu\text{-PhC}{\equiv}\text{CPh})(\eta^5\text{-}C_5Ph_5Pd)_2]$. Apparently, then, the acetate ion can promote the formation of **1** from $[(endo\text{-}C_4Ph_4OMe)PdCl]_2$. The total removal of chloride ion from $[(endo\text{-}C_4Ph_4OMe)PdCl]_2$ by the precipitation of MCl, where M = Ag or Tl on reaction of **8** with MOAc, leaves "*endo*-$C_4Ph_4ORPdOAc$" (**10**) in solution.

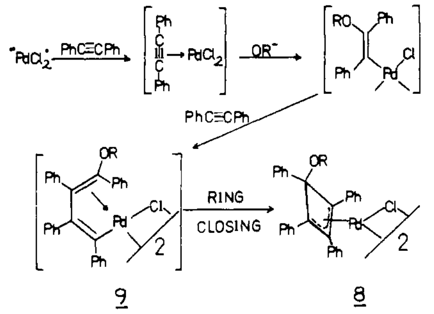
$$[(endo\text{-}C_4Ph_4OR)PdCl]_2 + 2MOAc \rightarrow 2MCl\downarrow + \text{“}endo\text{-}C_4Ph_4ORPdOAc\text{”} \qquad (2)$$

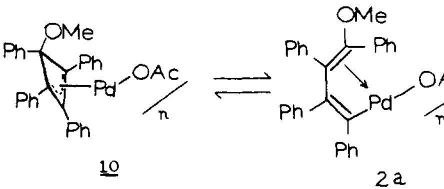
(the yield of AgCl is 96%)

OR = OMe, OEt; M = Ag, Tl

The species "*endo*-$C_4Ph_4OMePdOAc$" so produced can be isolated as an amorphous orange solid which has a carboxylate infrared spectrum typical of a bridging bidentate acetate (ν_{CO} asymm 1575 cm^{-1} and ν_{CO} symm 1403 cm^{-1}). The species in solution, however, is of ill-defined structure. The osmometric molecular weight in $CHCl_3$, 37 °C was much less than that expected of a dimer (762 g/mol observed compared to 1104 g/mol calculated for dimer). The ^1H NMR spectrum in $CDCl_3$ integrated according to the stoichiometry "*endo*-$C_4Ph_4OMePdOAc$", but was complex and temperature dependent, having no less than five methoxy resonances and two acetate resonances at −20 °C. By analogy with our studies of "*endo*-$C_4Ph_4OMePd(acac)$"[22] the observed complexity of the NMR spectrum of "*endo*-$C_4Ph_4OMePdOAc$" is consistent with an equilibrium between *endo*-alkoxycyclobutenyl **10** and ring-opened alkoxybutadienyl species of the type **2a**. For n = 2, several conformational isomers are possible.

Scheme III. Mechanism Proposed for the Formation of *endo*-Alkoxyltetraphenylcyclobutenylpalladium Chloride (8) from the Reaction of Diphenylacetylene with Bisbenzonitrilepalladium Chloride in Methanol or Ethanol[1,2]





Diphenylacetylene reacted with "*endo*-$C_4Ph_4OMePdOAc$" in methanol to give $[(\mu\text{-PhC}{\equiv}\text{CPh})(\eta^5\text{-}C_5Ph_5Pd)_2]$ (**1**), $PhC(OMe)_3$, HOAc, and elemental palladium (eq 3).

The reaction of "*endo*-$C_4Ph_4OMePdOAc$" with diphenylacetylene must involve the incorporation of part of the *endo*-C_4Ph_4OMe ligand into the product $[(\mu\text{-PhC}{\equiv}\text{CPh})(\eta^5\text{-}C_5Ph_5Pd)_2]$, as implied by the stoichiometry of eq 3, since

$$\begin{aligned}
&{}^3/_2[(endo\text{-}C_4Ph_4OMePdCl]_2 + 3AgOAc\\
&\quad\downarrow -3AgCl\\
&3\text{“}endo\text{-}C_4Ph_4OMePdOAc\text{”} + 3\ PhC{\equiv}CPh\\
&\quad\xrightarrow[MeOH]{} [(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_5Pd)_2]\\
&\quad + \underbrace{\{+ H^+ + C_4Ph_4OMe^-\}}_{\text{fate unknown}} + Pd(0) + 3HOAc + 2PhC(OMe)_3 \qquad (3)
\end{aligned}$$

the yield of **1** is too large to arise solely from the added diphenylacetylene. If this reaction proceeds as postulated in Scheme I, then the use of ethanol as the solvent for the reaction (eq 3) should lead to the formation of the mixed orthobenzoate, $PhC(OMe)(OEt)_2$. To test the validity of this prediction, this reaction was carried out along with the three other possible variations as shown in the equation

$$\begin{aligned}
&\text{“}endo\text{-}C_4Ph_4ORPdOAc\text{”} + PhC{\equiv}CPh\\
&\quad\xrightarrow{R^1OH} [(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_5Pd)_2]\\
&\qquad + 2PhC(OR)(OR^1)_2 + \ldots \qquad (4)
\end{aligned}$$

(i) OR = OMe, OR^1 = OMe
(ii) OR = OMe, OR^1 = OEt
(iii) OR = OEt, OR^1 = OMe
(iv) OR = OEt, OR^1 = OEt

In all cases, the predicted orthoester (1 mol/C_5Ph_5 ring and identified by ^1H NMR and mass spectroscopy) was produced in accord with the postulated mechanism. In the original

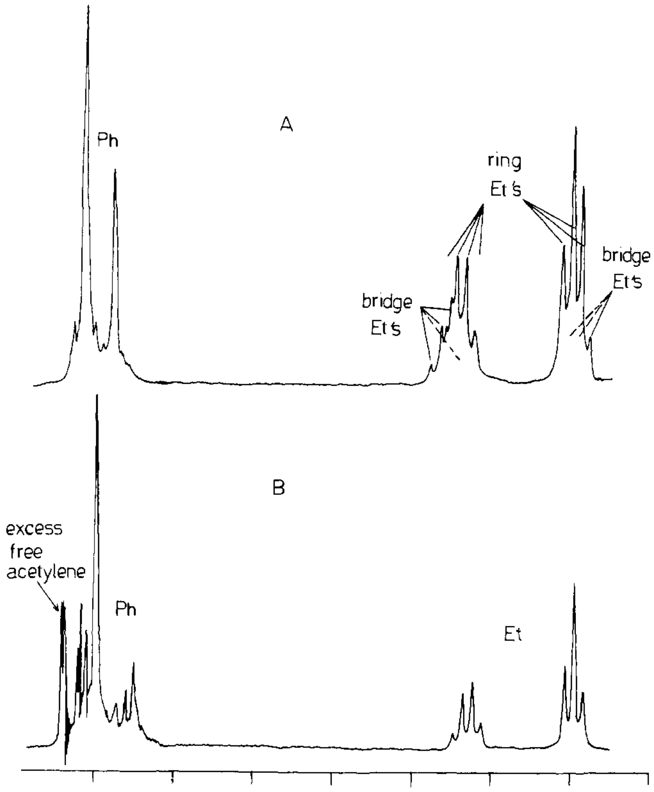


Figure 2. The ^1H NMR spectra in $CDCl_3$, 34 °C, of: (A) $[(\mu\text{-}EtC{=}CEt)(\eta^5\text{-}Ph_3Et_2C_5)_2Pd_2]$ (**11a**); and (B) $[(\mu\text{-}p,p'\text{-}BrC_6H_4C{\equiv}CC_6H_4Br)(\eta^5\text{-}Ph_3Et_2C_5)_2Pd_2]$ (**12g**) prepared from **11a** by reaction (eq 6) with excess $p,p'\text{-}BrC_6H_4C{\equiv}CC_6H_4Br$.

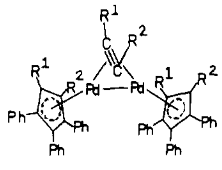
preparation of **1** from palladium acetate and diphenylacetylene in methanol (eq 1), it was noted that the ester, methyl benzoate, was always produced to some extent and it was suggested that its formation was due to the general-acid-catalyzed hydrolysis of the orthoester, $PhC(OMe)_3$. There is the possibility, however, that water can directly attack the intermediate **4** in Scheme I to yield "$PhC(OMe)(OH)_2$" (where OR = OMe), which will then spontaneously dehydrate to PhCOOMe. The use of 1:6 by volume aqueous acetone as solvent in eq 4 in place of R^1OH leads directly to the formation of **1** and PhCOOMe. Thus it appears that the ester, PhCOOMe, formed in the reaction of palladium acetate and diphenylacetylene (eq 1) can arise either by the hydrolysis of the orthoester, $PhC(OMe)_3$, or directly from the attack of a water molecule on the intermediate **4** in Scheme I.

(iv) **Preparation of $[(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}C_5Ph_3R^1R^2Pd)_2]$.** "*endo*-$C_4Ph_4ORPdOAc$" has been reacted with a series of disubstituted acetylenes $R^1C{\equiv}CR^2$ in alcohol (eq 5). On the basis of the proposed mechanism, Scheme I, the introduction of a new acetylene, $R^1C{\equiv}CR^2$, at intermediate **2** (Scheme I) should lead to the formation of complexes $[(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}C_5Ph_3R^1R^2Pd)_2]$ (**11**) structurally analogous to green compound **1**. For the series of alkyl and aryl disubstituted acetylenes listed for eq 5, this was found to be the case. For example, see reaction 5.

$$\text{“}endo\text{-}C_4Ph_4ORPdOAc\text{”} + R^1C{\equiv}CR^2 \xrightarrow{\text{alcohol}} 2PhC(OR)_3 + \mathbf{11} \qquad (5)$$

complex	11a	11b	11c	11d	11e	11f	11g	11h
R^1 =	Et	Ph	tBu	Et	p-MeOC$_6$H$_4$	p-tolyl	p-BrC$_6$H$_4$	Ph
R^2 =	Et	Me	Me	Me	p-MeOC$_6$H$_4$	p-tolyl	p-BrC$_6$H$_4$	Naphth

$EtC{\equiv}CEt$ (R^1, R^2 = Et) with "*endo*-$C_4Ph_4OMePdOAc$" in EtOH results in the slow precipitation of **11a** as purple prisms, mp 175–177 °C, which dissolve readily in organic solvents to give an intense royal blue solution. The visible spectrum of this solution in chloroform is similar to that of **1** with two strong absorptions at 598 and 374 nm. In $CDCl_3$ solution, the ^1H NMR spectrum of **11a** (shown in Figure 2) clearly indicates the presence of two sets of ethyl resonances in a 2:1 ratio assignable to the $\eta^5\text{-}C_5Ph_3Et_2$ and Et_2C_2 ligands, respectively. The mass spectrum confirmed the presence of these ligands (see Table I). Elemental analysis and an osmometric molecular weight determination (994 g/mol calcd; 916 g/mole found) are consistent with the formulation of **11a** as $[(\eta^5\text{-}C_5Ph_3Et_2)_2(\mu\text{-}Et_2C_2)Pd_2]$. Degradation of the complex **11a** with excess HCl leads to the isolation of $C_5Ph_3Et_2H$. Thus the product of eq 5, where R^1, R^2 = Et, is firmly established as $[(\mu\text{-}EtC{\equiv}CEt)(\eta^5\text{-}C_5Ph_3Et_2Pd)_2]$ (**11a**). In addition, the reaction mixture contained 2 mol of $PhC(OMe)(OEt)_2$ for each mole of **11a** produced. The analytical and spectroscopic data pertaining to the structural characterization of **11b–h** are given in Table I. The UV-visible spectrum of **11c** (R^1 = t-Bu, R^2 = Me) contained an extra absorption at ~480 nm which was attributed to a decomposition product, since the green colored species was unstable in this instance and could not be isolated pure in the solid state. Attempts to extend this reaction (eq 5) to acetylenes with nonaryl or alkyl substituents did not yield complexes which were analogous to the green compound **1**. Use of the acetylenes $R^1C{\equiv}CR^2$, where R^1, R^2 = H, $SiMe_3$, CF_3, or CMe_2OH, in eq 5 all led to decomposition. For R_1, R^2 = $SiMe_3$, this decomposition is probably due to the sensitivity of the Si–acetylene bond in alcoholic media.[28]



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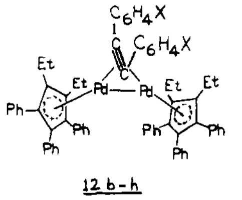
(v) **Exchange of the Bridgine Acetylene in the Complexes, $[(\mu\text{-}R^1C{\equiv}CR^1)(\eta^5\text{-}C_5Ph_3R^1R^2Pd)_2]$.** The complexes $[(\mu\text{-}RC{\equiv}CR)Co_2(CO)_6]$[29] and $[(\mu\text{-}RC{\equiv}CR)(\eta^5\text{-}C_5H_5\text{-}Ni)_2]$,[30,31] which are structural analogues of the complexes **1** and **11a–h** undergo a relatively facile bridging acetylene exchange reaction. The order of displacement proved to be: $CF_3C{\equiv}CCF_3 \gg MeOOCC{\equiv}CCOOMe > PhC{\equiv}CPh > PhC{\equiv}CH > HC{\equiv}CH \geq PhC{\equiv}CMe > MeC{\equiv}CH > MeC{\equiv}CMe$.[31] The corresponding palladium complexes **11** do not undergo such a displacement reaction under mild conditions. Replacement of the bridging acetylene by a less volatile acetylene was achieved, however, by heating the system in alcohol under reduced pressure.

$$[(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}C_5Ph_3R^1R^2Pd)_2] + RC{\equiv}CR \xrightarrow{\text{EtOH}} R^1C{\equiv}CR^2\uparrow + \underset{\mathbf{12}}{[(\mu\text{-}RC{\equiv}CR)(\eta^5\text{-}C_5Ph_3R^1R^2Pd)_2]} \qquad (6)$$

Completion of the reaction was determined by the constancy of λ_{max} in the visible spectrum of the reaction mixture. Displacing the bridging acetylene from the complex $[(\mu\text{-}Et_2C_2)(\eta^5\text{-}C_5Ph_3Et_2Pd)_2]$ (**11a**) by eq 6 with $PhC{\equiv}CPh$ yields a new compound in which the ^1H NMR resonance of the bridging acetylene ethyl groups has disappeared, leaving the resonance of the ring ethyl substituents unshifted and undiminished. During the bridging acetylene exchange reaction, the color of the reaction mixture changes visibly from blue green to green, corresponding to the difference in the visible spectra of reagent and product. The new green product can be isolated from this reaction, initially as a glass. Recrystallization from chloroform/methanol yielded green prisms with properties typical of the expected compound, $[(\mu\text{-}PhC{\equiv}CPh)(\eta^5\text{-}C_5Ph_3Et_2Pd)_2]$ (**12e**) (see Table I). The complexes **12a–i** were similarly prepared and characterized. In an attempt to establish the dependence of the color of the complexes on the nature of the bridging acetylene substituents, a series of complexes **12b–h** was generated by the bridge displacement reaction. The reaction was monitored for completion by visible and ^{1}H NMR spectroscopy as outlined for eq 6 above. The ^{1}H NMR spectra shown in Figure 2 of the reagent and product of the reaction of **11a** with $p,p'\text{-}BrC_6H_4C{\equiv}CC_6H_4Br$ are consistent with the displacement of the bridging 3-hexyne to yield the complex $[(\mu\text{-}p,p'\text{-}BrC_6H_4C{\equiv}CC_6H_4Br)(\eta^5\text{-}C_5Ph_3Et_2Pd)_2]$ (**12g**). In all cases, the complexes $[(\mu\text{-}p,p'\text{-}XC_6H_4C{\equiv}CC_6H_4X)(\eta^5\text{-}C_5Ph_3Et_2Pd)_2]$ (**12**) can be isolated as crystalline solids. From the visible spectra of the complexes summarized in Table I, it can be seen that both the high and low wavelength absorptions are shifted to longer wavelength with increased electron withdrawal by the bridging acetylene para substitutents, X. A plot of frequency vs. the Hammet constant σ_p gave a reasonably linear correlation for the high wavelength absorptions, but not with the lower wavelength absorption. Although a definite assignment of the electronic levels involved cannot be made, the green color of Allegra's Pd(I) dimers $[(\mu^6\text{-}C_6H_6)PdAlCl_3X]_2$, X = Cl or $AlCl_4$, may indicate a similar visible spectrum in which case the electrons of the palladium(I)–palladium(I) bond would be implicated for the longer wavelength absorption (i.e., perhaps a Pd–Pd $\sigma \rightarrow \sigma^*$ transition).



12 b–h

(vi) **The Synthesis of Bis(η^5-penta-*p*-tolylcyclopentadienyl)(μ-RC≡CR)dipalladium(I) Complexes.** Attempts to prepare $[\{\eta^5(p\text{-tolyl})_5C_5\}_2(\mu\text{-}p\text{-tolyl}_2C_2)Pd_2]$ (**13a**) by the reaction of di-*p*-tolylacetylene with palladium acetate in methanol gave the required product **13a** as a green precipitate in very low yield (ca. 5%). The overall yield of **13a** is increased to 50% (based on Pd incorporation into the complex) by first preparing "(*endo*-methoxytetra-*p*-tolylcyclobutenyl)palladium acetate" which can then be reacted with various acetylenes to give cyclopentadienyl products, e.g., **13a,b** (see Table I). The complexes **13a** and **b** are considerably more soluble than those derived from diphenylacetylenes.

(vii) **Preparation of the Complexes (*endo*-η^3-4-alkoxy-1,2,3,4-tetraphenylcyclobutenyl)(η^5-dicarbomethoxytriphenylcyclopentadienyl)palladium(II).** The reaction of aryl and alkyl disubstituted acetylenes with "*endo*-$C_4Ph_4ORPdOAc$" in alcohol (eq 5) yields the complexes $[(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}C_5Ph_3R^1R^2Pd)_2]$ (**11**). The same reaction with $MeOOCC{\equiv}CCOOMe$, however, leads to the formation of red needles, which by analysis and molecular weight characterize as $[(C_4Ph_4OR)Pd\{C_5Ph_3(COOMe)_2\}]$, OR = OMe (**14a**) or OEt (**14b**). The infrared of the carboxyl ester group in these compounds has frequencies (ν_{CO}, 1730 and 1720 cm^{-1} for **14a** and 1720 cm^{-1} for **14b**) consistent with uncoordinated carbomethoxy groups. The C=O stretching frequency expected of coordinated carbomethoxy (1638 cm^{-1})[24,32] is absent. The mass spectra of **14a** and **b** contain major peaks for the ions $C_5Ph_3(COOMe)_2H^+$ and $(C_4Ph_4OR\text{-}H)^+$ and closely resemble "*endo*-C_4Ph_4OR" complexes in their fragmentation pattern (especially for the low mass fragments). The reaction of **14a** or **b** with RC≡CR (R = aryl, alkyl) in alcohol leads to the formation of green solution species. Since only *endo*-alkoxytetraphenylcyclobutenyl species have been found to react with acetylenes to give green compounds, the complexes **14a** and **b** have been assigned the structure (*endo*-η^3-4-alkoxytetraphenylcyclobutenyl)(η^5-dicarbomethyoxytriphenylcyclopentadienyl)palladium(II) as shown with the ^{1}H NMR of **14b**, in Figure 3. From the analysis of other products formed during the preparation of **14a–b** it was apparent that one ester or orthoester is produced for each dicarbomethoxytriphenylcyclopentadienyl ligand formed. It is possible that failure to form a complex structurally analogous to **11** may be due to the unsatisfactory bridging ability of this acetylene, $MeOOCC{\equiv}CCOOMe$ (as was noted in the bridge displacement reactions). On the basis of earlier work a reasonable reaction equation for the preparation of **14** is eq 7)

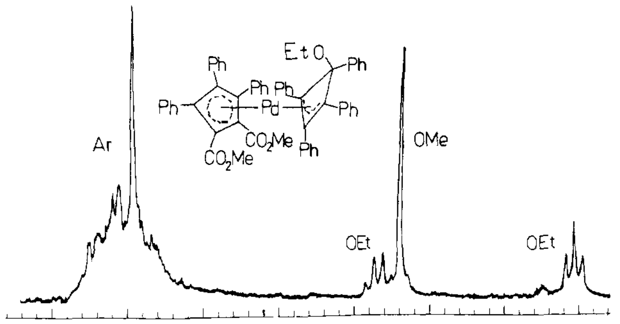


Figure 3. ^{1}H NMR spectrum in $CDCl_3$, 34 °C, of **14b**.

$$2\,\text{“}endo\text{-}C_4Ph_4ORPdOAc\text{”} + MeOOCC{\equiv}CCOOMe \xrightarrow{2R'OH} 2HOAc + xPhCO_2R + (1-x)PhCO_2R^1 + Pd(0) + (endo\text{-}C_4Ph_4OR)Pd\{C_5Ph_3(COOMe)_2\} \quad (7)$$

and the yields shown in the Experimental Section have been determined on the basis of this stoichiometry.

Besides the products shown in eq 7 the reaction also produces a considerable amount of dicarbomethoxytriphenylcyclopentadiene. The formation of this compound may arise by the decomposition of **14a–b** in the acidic reaction mixture and/or by protonation of $C_5Ph_3(COOMe)_2^-$, which may be an intermediate in the formation of **14a–b**. From the analysis of the reaction products, it appears that the hydrolysis reactions which produce the ester are very efficient in this instance. Even when the methanol solvent is specially dried, the yield of the orthoester $PhC(OMe)_2(OEt)$ is small relative to the esters PhCOOEt and PhCOOMe. The presence of PhCOOMe can only be accounted for by the hydrolysis of the orthoester, but PhCOOEt can arise directly from the production of **14a–b** as well, as discussed previously. Degradation of the complexes $[(endo\text{-}C_4Ph_4OR)Pd\{C_5Ph_3(COOMe)_3\}]$, where OR = OMe and OEt, in $CDCl_3$ with HCl gave the products ROH, $C_5Ph_3(COOMe)_2H$, and $[(\eta^4\text{-}C_4Ph_4)PdCl_2]_2$ as reported by Maitlis[33] for $[(endo\text{-}C_4Ph_4OR)PdC_5H_5]$.

(viii) **The Reactivity of $[(\eta^5\text{-}Ph_5C_5)_2(\mu\text{-}Ph_2C_2)Pd_2]$.** Complex **1** is quite inert to group 5 donor ligands such as Ph_3P, bpy, *o*-phen, diphos, or $(MeO)_3P$. Refluxing **1** in neat pyridine for 5 h gave a brown reaction mixture from which pentaphenylcyclopentadiene could be isolated. Other reagents such as 2,5-norbornadiene, methylacetylene dicarboxylate, hexaflurobut-2-yne, carbon monoxide, and $Fe(CO)_5$ failed to react with **1**.

Complex **1** did react quite readily with nitric oxide in a $CHCl_3$ solution

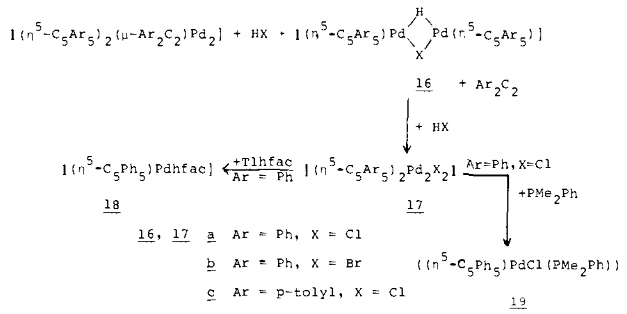
$$[(\eta^5\text{-}C_5Ar_3R^1R^2)_2(\mu\text{-}R^1R^2C_2)Pd_2] + 2NO \rightarrow \underset{\mathbf{15}}{[(\eta^5\text{-}C_5Ar_3R^1R^2)PdNO]} + R^1R^2C_2 \quad (8)$$

15a, Ar = $R^1 = R^2$ = Ph; ν_{NO} 1775 cm^{-1}
15b, Ar = $R^1 = R^2$ = *p*-tolyl; ν_{NO} 1756 cm^{-1}
15c, Ar = Ph; $R^1 = R^2$ = Et; ν_{NO} 1755 cm^{-1}

to yield the nitrosyl complex $[(\eta^5\text{-}Ph_5C_5)PdNO]$ (**15a**), isolated as a diamagnetic, purple solid, and diphenylacetylene. Complex **15a** exhibits ν_{NO} at 1775 cm^{-1} in excellent agreement with the value of 1789 cm^{-1} reported by Fisher for $[(\eta^5\text{-}C_5H_5)PdNO]$.[34,35] As previously noted in other studies of pentasubstituted cyclopentadiene complexes[36,37] compound **15a** is considerably more stable than its unsubstituted analogue, being indefinitely stable at room temperature under N_2. The unsubstituted analogue $[(\eta^5\text{-}C_5H_5)PdNO]$ is reported to be a red oil unstable at room temperature even under an atmosphere of argon.[34,35] Similarly, reaction of **13a** or **11a** with nitric oxide gave **15b** and **15c,** respectively. The complexes **15a–c,** while relatively stable in the solid, are unstable with respect to oxygen and moisture in solution.

The acids HCl, HBr, H_2SO_4, HNO_3, and $HOOCCF_3$ all cause the rapid destruction of the green compound **1** in solution with the color changing from green through purple to yellow. The stoichiometry of this reaction with the acids HCl and HBr was found to be different than that for other strong acids such as $HOOCCF_3$. Only a 1 molar equiv of HCl or HBr is required to destroy the green color ($\lambda_{668\ nm}$) of a chloroform solution of **1** (or **13a**) while 2 mol of $HOOCCF_3$/mol of **1** are required to affect the disappearance of the absorption at 668 nm. In the HCl reaction, the solution turns purple due to an absorption at 560 nm which maximizes at a ratio of 1:1 and disappears at a ratio of HCl/**1** of 2:1 to yield a deep yellow solution. From this latter solution the palladium(II) dinuclear complex $[(\eta^5\text{-}C_5Ph_5)_2Pd_2Cl_2]$ (**17a**) can be readily isolated (as a yellow brown crystalline solid in nearly quantitative yield) and structurally characterized (see Scheme IV). **17b** and **17c** were prepared similarly. The hfac derivative **18** and the phosphine complex **19** were readily obtained from **17a** as shown in Scheme IV. When dry HCl in $CHCl_3$ or C_6H_6 was added to an equimolar solution of green compound **1** on a reaction scale, a purple precipitate was formed which analyzed as $[(\eta^5\text{-}C_5Ph_5)_2Pd_2HCl]$ (**16a**) on the basis of its C and H content (but seemed to have an erratic Cl content) mass spectrum and molecular weight (see Table II). The visible spectrum of the precipitate had a major band at 560 nm ($\epsilon_M \sim 7000$ M^{-1} cm^{-1}). Diphenylacetylene was also isolated from the reaction. A similar reaction of **1** with HBr gave **16b,** and reaction of **13a** with HCl gave **16c.** While the stoichiometry of the reactions outlined in Scheme IV are reasonably defined the formulation of **16a–c** as bridging hydrido species is tentative as all attempts to locate a high-field resonance in their ^1H NMR spectra have failed. However, in a recent communication, Green et al.[38] have structurally characterized $[(Cy_3P)_2Pt_2(SiEt_3)_2(\mu\text{-}H)]$, although no hydrido resonance in the ^1H NMR of this and related μ-hydrido complexes were observed. The proposed structures **16a–c** receive further support from the existence of structurally well-defined analogues $[(\eta^5\text{-}C_5Me_5)_2M_2(\mu\text{-}H)Cl_3]$ where M = Rh or Ir.[39] The rhodium complex is also purple. The complexes **16a–c** decomposed slowly in hexane solution, depositing elemental palladium in 24–36 h at room temperature.[40]

Scheme IV



Attempts to synthesize analogues to **16a–c** starting from $[(\eta^5\text{-}C_5Ph_4Me)_2(\mu\text{-}PhC{\equiv}CMe)Pd_2]$ or from $[(\eta^5\text{-}C_5Ph_3Et_2)_2(\mu\text{-}EtC{\equiv}CEt)Pd_2]$ gave purple solution species of only transient stability.

Experimental Section

^1H NMR spectra were recorded on Varian Associates Model A56/60D or T60 spectrometers. UV–visible spectra were recorded on a Unican SP 800. Mass spectra were recorded on a Bell and Howell Model 21-490 spectrometer at an ionization energy of 70 eV. Molecular weights were measured using a Mechrolab Model 301A vapor pressure osmometer. Melting points were determined on a Kofler hot stage and are corrected.

The di-μ-chlorobis(*endo*-η^3-4-alkoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) complexes, where alkoxy is methoxy or ethoxy, were prepared as described by Maitlis et al.[27]

The orthoester, $PhC(OMe)_3$, was identified by a comparison of its physical and spectral properties with an authentic sample.[41] The other orthoesters, $PhC(OMe)_{3-x}(OEt)_x$, x = 1, 2, 3, were identified by their ^1H NMR spectra and by their mass spectral fragmentation patterns, which were consistent with that found for $PhC(OMe)_3$. In all cases, the highest *m/e* peak did not correspond to the parent ion, but to the ion $PhC(OR)(OR^1)^+$, which presumably arises from the orthoester by the loss of an alkoxy group.

Complex 1: μ-Diphenylacetylene-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(I). Diphenylacetylene (18.5 g) was added to a suspension of diacetatopalladium(II) (11.0 g) in methanol (175 mL). The mixture was stirred at room temperature for 24 h. The resultant green precipitate was filtered, washed with methanol, and air dried. Chromatography using a benzene eluate on an alumina column gave the required product as dark green prisms (from benzene/hexane), yield 10.2 g.

Stoichiometry of the Preparation of Complex 1. Palladium acetate (0.999 g, 4.46 × 10^{-3} mol) and diphenylacetylene (2.784 g, 1.56 × 10^{-2} mol) were stirred together for 4 h in methanol which had been freshly distilled off magnesium methoxide.[42] The green precipitate (1.57 g) was collected by filtration and washed with methanol. The filtrate and washings were evaporated to dryness under reduced pressure. The residual oil was dissolved in exactly 5 mL of $CDCl_3$ and an aliquot was taken for ^1H NMR. Integration against a known concentration of added $Me_2C{=}CMe_2$ gave a combined yield of 1.66 × 10^{-3} mol of PhCOOMe and $PhC(OMe)_3$. The concentration of complex **1** in the green precipitate, isolated above, was 8.61 × 10^{-4} mol on the basis of λ_{max} 668 nm, ϵ_M 30 200 M^{-1} cm^{-1} in $CHCl_3$.

Reaction of 1 with excess HCl. Reaction of **1** with excess HCl in chloroform gave a reddish yellow solution from which elemental palladium was removed by columning the solution through alumina. The eluate was isolated by evaporation and extracted with a hot hexane/EtOH (4:1) mixture to give a pale yellow solution from which impure pentaphenylcyclopentadiene was recovered as a pale yellow solid. Sublimation [194 °C (0.05 mmHg)] gave colorless needles which sublimed at 242–245 °C. The sublimed prismatic needles so obtained melted sharply at 256–259 °C (lit. mp 244–246 °C).[43] Anal. Calcd for C_5Ph_5H: C, 94.17; H, 5.83. Found: C, 94.19; H, 5.86. Molecular weight, osmometrically in $CHCl_3$, 435 g/mol. Calcd for C_5Ph_5H; 446 g/mol. The mass spectrum consisted of the fragmentation pattern for the ion $C_5Ph_5H^+$, *m/e* 446, and the ^1H NMR in $CDCl_3$ had the resonances δ 5.05 (1, ring proton) and 6.8–7.2 (25 phenyl protons).

Preparation of "*endo*-$C_4Ph_4OMePdO_2CCH_3$", complex 10 ⇌ 2a. Di-μ-chloro-bis(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) (0.551 g) and silver acetate (0.174 g) were stirred in dichloromethane (30 mL) for 3.5 h. Silver chloride (0.146 g, 97% yield) was separated by filtration. The filtrate was evaporated down to an orange solid, which was recrystallized from CH_2Cl_2/hexanes to give "*endo*-$C_4Ph_4OMePdOOCCH_3$", (0.27 g, 47% yield). The molecular weight (osmometrically in $CHCl_3$, 37 °C): found, 762 g/mol; calcd, 552 g/mol. ^1H NMR spectrum in $CDCl_3$ at 34 °C: integration of methoxy to acetate resonances is 1:1, but the spectrum is temperature dependent and too complex to assign to structures.

Preparation of 1 from 10 ⇌ 2a. Di-μ-chloro-bis(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) (0.388 g, 3.66×10^{-4} mol) and silver acetate (0.122 g) were stirred in CH_2Cl_2 for 2 h. The precipitated silver chloride (0.099 g, 95%) was removed by filtration and the filtrate was evaporated to an orange solid which was redissolved in methanol (20 mL) with diphenylacetylene (0.088 g). After 24 h, the green precipitate was collected. The yield of **1** by visible spectroscopy was 1.65×10^{-4} mol (68% yield based on three reagent moles for 2 mol product). The yield of PhCOOMe + $PhC(OMe)_3$ based on the integration of the ^1H NMR spectrum of the reaction mixture against a known quantity of $Me_2C{=}CMe_2$ was 3.22×10^{-4} mol.

Preparation of complexes 11, $[(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}Ph_3R^1R^2C_5)_2Pd_2]$: e.g., μ-Hex-3-yne-bis(η^5-diethyltriphenylcyclopentadienyl)dipalladium(I) (11a). Di-μ-chloro-bis(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) (0.393 g, 3.66×10^{-4} mol) and silver acetate (0.126 g) were stirred in CH_2Cl_2 (10 mL) for 2.5 h. The silver chloride precipitate was removed by filtration and the solution evaporated down to an orange glass, which was taken up in warm ethanol (30 mL) and filtered. 3-Hexyne (0.999 g) was added to the filtrate. On standing overnight purple prisms of **11a** (30% yield) formed in the deep blue solution along with some elemental palladium. The orthoester isolated from this reaction was $PhC(OMe)(OEt)_2$.

Degradation of **11a** in chloroform solution with excess gaseous HCl caused a rapid change in color from blue to yellow brown. The solution was columned through alumina and evaporated to dryness. The pale yellow residue gave a parent ion in the mass spectrum corresponding to $C_5Ph_3Et_2H^+$ (*m/e*, 350). The ^1H NMR spectrum of this solid in $CDCl_3$ consisted of: Ar, $\delta \sim 6.8$–7.4; H, $\delta \sim 4.37$; and Et protons $\delta \sim 0.7$–2.7 in the ratio expected for $C_5Ph_3Et_2H$. The complexity of the resonances suggests that various isomers of diethyltriphenylcyclopentadiene are present.

μ-Phenylmethylacetylene-bis(η^5-methyltetraphenylcyclopentadienyl)dipalladium(I) (11b). Di-μ-chloro-bis(*endo*-η^3-4-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) (0.817 g) and silver acetate (0.258 g) were stirred for 2 h in CH_2Cl_2 (12 mL). The silver chloride precipitate was filtered off and the filtrate evaporated to a yellow solid, which was taken up in dry methanol and filtered. Phenylmethylacetylene (0.258 g) was added to the filtrate (22 mL), which precipitated **11b** as a purple solid from a bluish green solution after 24 h (yield, 0.413 g; 75%). The mother liquor contained $PhC(OEt)(OMe)_2$. Degradation of **11b** with excess HCl in chloroform resulted in a yellow reaction mixture. The mixture was columned through alumina and the solvent evaporated off to leave an off-white solid. Recrystallization gave C_5Ph_4MeH as a white solid, mp 171–174 °C. The parent peak in the mass spectrum was $C_5Ph_4MeH^+$ (*m/e* 384). The molecular weight (osmometrically in chloroform at 37 °C) was 389 g/mol (compared to 384 g/mol required for C_5Ph_4MeH). ^1H NMR in $CDCl_3$ indicates the presence of at least two isomers of methyltetraphenylcyclopentadiene. The complexes **11c–h** were prepared in analogous fashion to **11b**.

Bridge Displacement Reactions: the Preparation of the Complexes $[(\mu\text{-}R^3C{\equiv}CR^4)(\eta^5\text{-}Ph_3R^1R^2C_5)_2Pd_2]$. The bridging acetylene can be displaced from the complexes **11** by a less volatile acetylene $RC{\equiv}CR$ in hot ethanol under reduced pressure. Thus μ-$PhC{\equiv}CMe$ in **11b** has been displaced by $PhC{\equiv}CPh$, and μ-$EtC{\equiv}CEt$ in **11a** has been displaced by $PhC{\equiv}CPh$, $PhC{\equiv}CMe$, *p,p'*-$MeOC_6H_4C{\equiv}CC_6H_4OMe$, *p,p'*-$MeC_6H_4C{\equiv}CC_6H_4Me$, *p,p'*-$FC_6H_4C{\equiv}CC_6H_4F$, *p,p'*-$ClC_6H_4C{\equiv}CC_6H_4Cl$, *p,p'*-$BrC_6H_4C{\equiv}CC_6H_4Br$, and *p,p'*-$NO_2C_6H_4C{\equiv}CC_6H_4NO_2$. One example of the procedure follows.

μ-Diphenylacetylene-bis(η^5-diethyltriphenylcyclopentadienyl)dipalladium(I). Diphenylacetylene (0.328 g) and μ-diethylacetylene-bis(η^5-diethyltriphenylcyclopentadienyl)dipalladium(I) (0.177 g) were dissolved in 1:1 dry methanol/dichloromethane to give a blue solution (10 mL). The mixture was evaporated almost to dryness on the steam bath under reduced pressure. The solvent was replaced with ethanol/chloroform (10 mL) and evaporated to dryness at ~80 °C under reduced pressure. A ^1H NMR of the blue-green residue in $CDCl_3$ indicated the total removal of the bridging acetylene ethyl resonances. The solid was columned as a benzene solution through Florisil and recrystallized from chloroform/methanol to give **12e** as green prisms (40% yield).

Preparation of *endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl-η^5-dicarbomethoxytriphenylcyclopentadienylpalladium(II), complex 14a. Di-μ-chloro-bis(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) (0.286 g) and silver acetate (0.097 g) were stirred for 4 h in CH_2Cl_2. The silver chloride was filtered off and the filtrate evaporated to a yellow solid which was redissolved in warm methanol (30 mL) and filtered. Dimethylacetylene dicarboxylate, $MeOOCC{\equiv}CCOOMe$ (0.10 g), was added to the filtrate which on standing overnight yielded **14a** as red prisms in 56% yield.

***endo*-η^3-4-Ethoxy-1,2,3,4-tetraphenylcyclobutenyl-η^5-dicarbomethoxytriphenylcyclopentadienylpalladium(II), complex 14b.** This complex was prepared from di-μ-chloro-bis(*endo*-η^3-4-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) as described above for the methoxy complex except that the solvent used was ethanol in this case. The product was isolated as red prisms (27% yield). The reaction mixture in this case was found to contain $[C_5Ph_3(COOMe)_2H]$ in 41% yield.

Determination of Yields for the Preparation of $[(endo\text{-}\eta^3\text{-}C_4Ph_4OMe)Pd(\eta^5\text{-}C_5Ph_3(COOMe)_2)]$. Di-$\mu$-chloro-bis(*endo*-$\eta^3$-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) (0.383 g) and silver acetate (0.117 g) were stirred in CH_2Cl_2 for 5 h then filtered and evaporated to dryness. The residue was dissolved in *dry* methanol, filtered, and $MeOOCC{\equiv}CCOOMe$ (0.121 g) added to the filtrate. After 24 h red needles of $[(endo\text{-}\eta^3\text{-}C_4Ph_4OMe)Pd\{\eta^5\text{-}C_5Ph_3(COOMe)_2\}]$ were isolated (0.154 g). The methanol insoluble residue not involved in reaction with $MeOOCC{\equiv}CCOOMe$ was reacted with HCl in CH_2Cl_2 solution to yield the (η^4-tetraphenylcyclobutadiene)palladium chloride, $[(\eta^4\text{-}C_4Ph_4)PdCl_2]_2$, as a red solid (0.107 g). This enabled the computation of the amount of "*endo*-$C_4Ph_4OMePdOAc$" actually involved in the reaction with $MeOOCC{\equiv}CCOOMe$. The yield of $[(endo\text{-}\eta^3\text{-}C_4Ph_4OMe)Pd\{\eta^5\text{-}C_5Ph_3(COOMe)_2\}]$ on this basis was 66.7%.

The mother liquor from this reaction was inspected by ^1H NMR spectroscopy and found to contain $C_5Ph_3(COOMe)_2H$ (22.3% yield). The total cyclopentadienyl ring formation was 66.7 + 22.3 = 89%. The total yield of $PhC(OMe)_2(OEt)$ + PhCOOMe + PhCOOEt by ^1H NMR spectroscopy was 93.5%, which gives 1 mol of esters formed per $C_5Ph_3(COOMe)_2^-$ ring.

Degradation of $[(endo\text{-}\eta^3\text{-}C_4Ph_4OMe)Pd\{\eta^5\text{-}C_5Ph_3(COOMe)_2\}]$. $[(endo\text{-}\eta^3\text{-}C_4Ph_4OMe)Pd\{\eta^5\text{-}C_5Ph_3(COOMe)_2\}]$ (0.106 g) in $CDCl_3$ (1.5 mL) had HCl bubbled through it for 5 min. Both $C_5Ph_3(COOMe)_2H$ and MeOH were evident by ^1H NMR spectroscopy. The sample was centrifuged and filtered to remove the orange precipitate formed (0.037 g). The filtrate was evaporated to dryness to yield a pale orange residue, which was extracted with hot hexanes to leave more orange precipitate (0.016 g). The hexane extractions yielded a white solid, mp 152–160 °C, in 90% yield based on $C_5Ph_3(COOMe)_2H$. Mol wt required, 410 g/mol; found, mol wt (osmometrically in $CHCl_3$, 37 °C) 481 g/mol; mass spectrum, *m/e* 410. ^1H NMR spectrum: Ar protons, broad resonance at ~7.15 ppm; COOMe protons, singlets at 3.63 and 3.56 ppm in a 1:1 ratio; and ring H a singlet at 5.07 ppm. The orange solid, mp 295–300 °C (0.054 g, 91.8% yield), was identified as di-μ-chlorodichloro-bis(η^4-tetraphenylcyclobutadiene)dipalladium(II), by its physical properties and reactivity with methanol to yield di-μ-chloro-bis(*exo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II).[44]

Degradation of the ethoxy analogue $[(endo\text{-}C_4Ph_4OEt)Pd\{\eta^5\text{-}C_5Ph_3(COOMe)_2\}]$ by the same procedure gave analogous results.

Reaction of *1* with Nitric Oxide: the Preparation of η^5-Pentaphenylcyclopentadienylnitrosylpalladium(I) (15a). Nitrogen was bubbled through a stirred chloroform solution (50 mL) of **1** (2.22×10^{-4} mol) for 15 min. Then nitric oxide was bubbled through the solution until the color had changed from green to magenta. The excess nitric oxide was removed from solution by bubbling nitrogen through it. Evaporation of the solvent left a purple solid residue, which was extracted with hot hexanes under nitrogen to remove diphenylacetylene. The residual purple solid (0.10 g, 40% yield) was assigned the formula $[(\eta^5\text{-}C_5Ph_5)PdNO]$. It was soluble in organic solvents, insoluble in water, and of limited solubility in methanol. Complexes **15b** and **15c** were prepared in a similar manner.

μ-Chloro-μ-hydrido-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (16a). A solution of dry HCl in chloroform (1.6 mL of 0.269 M) was added to a stirred solution of μ-diphenylacetylene-bis(η^5-

pentaphenylcyclopentadienyl)dipalladium(I) (4.29×10^{-4} mol) in A.C.S. chloroform (0.75% ethanol added; 99 mL). The solution turned purple and on reducing the volume **16a** was precipitated as a purple solid (58%). Evaporation of the mother liquor to dryness followed by hexane extraction of the residue yielded diphenylacetylene (>90%). Complexes **16b** and **16c** were prepared similarly.

Di-μ-chloro-bis(η^5-pentaphenylcyclopentadienyl)dipalladium(II) (17a). To a solution of complex **1** (0.976 g) in chloroform (50 mL) was added 4.6 mL of a chloroform solution of HCl (0.34 M). The reaction was stirred for 30 min, the solution reduced in volume to 10 mL, *n*-pentane (70 mL) added, and the solution cooled to 0 °C. The complex **17a** precipitate from the solution as a brown solid (0.761 g; 85%). The complexes **17b** and **17c** were prepared similarly.

The reaction of **17a** with an equimolar quantity of Tl(hfac) in CH_2Cl_2 gave complex **18** as an orange glass (80% yield).

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Reduction Studies on Mixed Chelate Complexes

Robert J. Balahura* and Nita A. Lewis

Contribution from the Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.
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Abstract: The Cr^{2+} reductions of the complexes $[Co(en)(ptdn)_2]^+$, $[Co(en)_2(ptdn)]^{2+}$, and $[Co(en)_3]^{3+}$ have been studied. The reaction of $[Co(en)(ptdn)_2]^+$ proceeded by three pathways: inner-sphere monobridged ($k^{25 °C} = (2.5 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 13.7 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -24 \pm 3$ eu), inner-sphere dibridged ($k^{25 °C} = (2.1 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 13 \pm 1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -28 \pm 5$ eu), and outer sphere ($k^{25 °C} = (2.0 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 10 \pm 2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -36 \pm 7$ eu); $\mu = 1.0$ M ($LiClO_4$). The $[Co(en)_2(ptdn)]^{2+}$ complex was reduced by Cr^{2+} with $k^{50 °C} = 5.7 \times 10^{-5}$ M^{-1} s^{-1}, $\mu = 1.0$ M ($LiClO_4$). This reaction was shown to occur partially by an inner-sphere path. For $[Co(en)_3]^{3+}$ only an outer-sphere path is possible and $k^{50 °C} = 1.1 \times 10^{-4}$ M^{-1} s^{-1}, $\mu = 1.0$ M ($LiClO_4$). Rate trends within the series $[Co(ptdn)_3]$, $[Co(en)(ptdn)_2]^+$, $[Co(en)_2(ptdn)]^{2+}$, and $[Co(en)_3]^{3+}$ as well as within the analogous oxalato-Co(III) complexes are discussed in terms of ligand field effects.

There do not appear to have been many systematic studies of redox reactions of mixed chelate compounds in which the number of chelate rings of one kind is varied within a series.[1] Such studies are hampered by synthetic difficulties involved in preparing the full series and by problems of solubility in the case of many ligands.

We have recently been interested in the reactions of mixed chelate compounds, particularly those involving pentane-2,4-dionato and derivatives of this ligand.[2] The investigation of rate trends throughout a series of mixed chelates was especially interesting from two points of view. First, the possibility that the changes in rate constants would vary systematically, based on ligand field effects,[3] could be determined, and second, the differences in the detailed mechanism of electron transfer through chelates in general, a rather neglected topic in the study of redox chemistry, could be elucidated.