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CYCLOBUTADIENE–METAL COMPLEXES
XII*. SYNTHESES AND SOME REACTIONS OF *para*-SUBSTITUTED-(TETRAPHENYLCYCLOBUTADIENE)PALLADIUM HALIDES

D. F. POLLOCK AND P. M. MAITLIS**
Chemistry Department, McMaster University, Hamilton, Ontario (Canada)

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SUMMARY

Cyclobutadienepalladium halide complexes of the type $[R_4C_4PdX_2]_2$ (V, R = *p*-MeC_6H_4, *p*-$MeOC_6H_4$) have been prepared from the appropriate acetylenes (RC_2R) and $(PhCN)_2PdCl_2$. Ligand-transfer reactions to give $R_4C_4Fe(CO)_3$, $[R_4C_4NiX_2]_2$, $[R_4C_4PdC_5H_5]^+$ and $[R_4C_4NiC_5H_5]^+$ as well as reactions to give the cyclooctatetraenes (R_8C_8) and the cyclopentadienones, R_4C_5O, were carried out. The presence of a π-cyclobutadiene ring in complexes of this type, with R = *p*-XC_6H_4, was shown by the appearance of an AB quartet arising from the *o*- and *m*-aromatic protons in the NMR spectrum. The *p*-anisyl complex (V, R = *p*-$MeOC_6H_4$), did not give a cyclobutenyl complex with ethanol whereas the complexes (V) with R = Ph, *p*-ClC_6H_4 and *p*-MeC_6H_4 did.

INTRODUCTION

We have previously discussed the preparation of (tetraphenylcyclobutadiene)-palladium halides[1,2] and their *p*-chlorophenyl analogs[3] from the appropriate acetylenes. In this paper we present results on the reactions of some other *p,p'*-disubstituted diphenylacetylenes with palladium chloride to give the appropriate cyclobutadiene complexes as well as details of a number of new complexes arising from them.

RESULTS AND DISCUSSION

The reactions which have been carried out are summarised in Scheme 1. For completeness, some of those already described for diphenylacetylene (Ia) and bis-(*p*-chlorophenyl)acetylene (Ib) and their related complexes are included. Complexes not previously described are those derived from di-*p*-tolylacetylene (Ic) and di-*p*-anisylacetylene (Id); analytical data are presented in Table 2.

The reactions of the acetylenes (Ic) and (Id) with $(PhCN)_2PdCl_2$ in benzene paralleled those of (Ia) and (Ib); in every case the products were the benzenes (III) and the cyclobutadiene complexes (II). The relative yields were dependent on the

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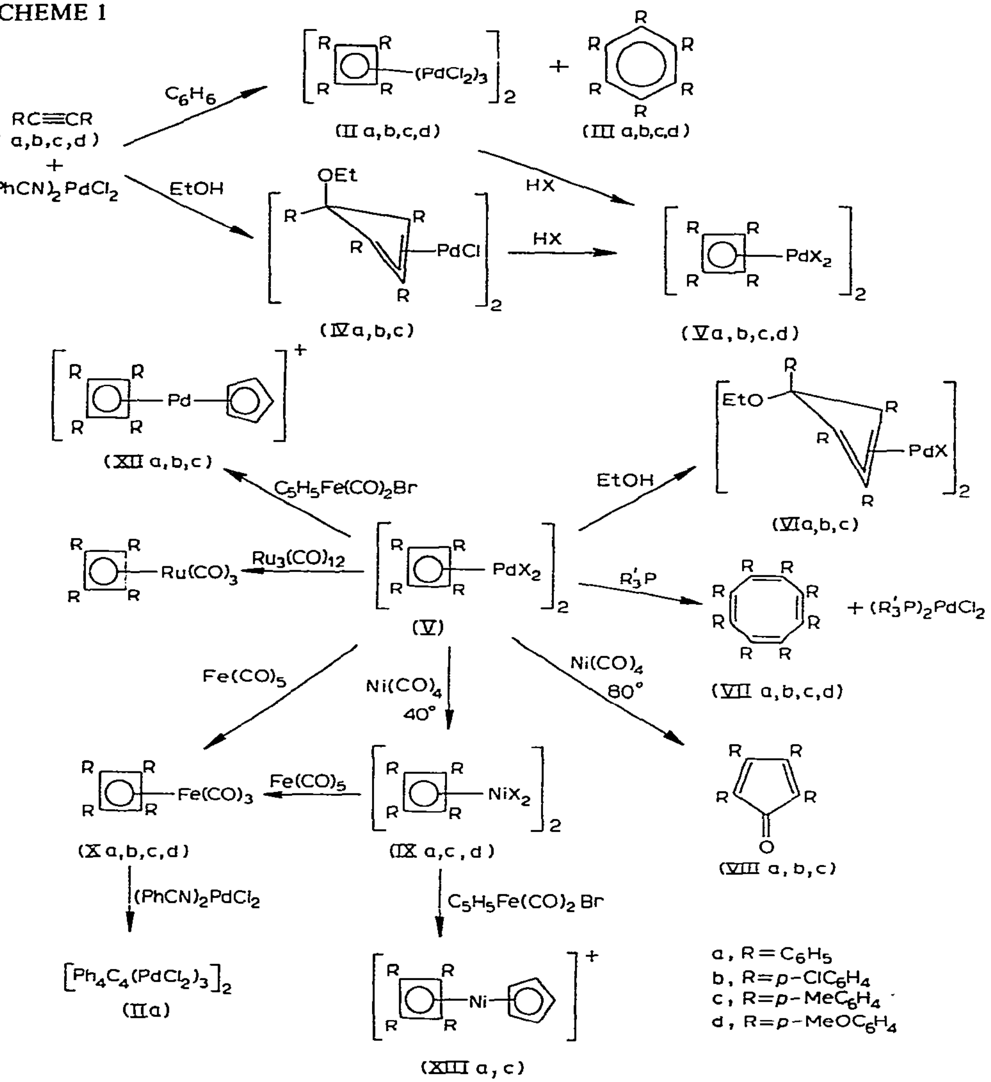
* For Part XI see ref. 12.
** Fellow of the Alfred P. Sloan Foundation and author to whom any correspondence should be addressed.

SCHEME 1



ratios of reactants and on the mode of addition; those quoted in Table 1 were obtained on slow addition of one mole of the acetylene to a slight excess of $(PhCN)_2PdCl_2$, both dissolved in large volumes of benzene. Within the limits of accuracy of these results, there does not seem to be any significant difference between the various acetylenes and therefore we suggest that electronic effects are not of prime importance in this reaction.

The structures of the complexes (II) have already been commented on[3]; we presume them to have $PdCl_2$ units catenated between two cyclobutadiene rings. The complexes (II) were converted to the "normal" cyclobutadiene complexes (V) either by reaction with the hydrogen halide (HX) in methylene chloride or, as described by Hüttel and Neugebauer[4], using dimethylformamide and HX. The latter procedure gave higher yields and was more convenient. The cyclobutadiene complexes (Vb,c, X = Br) were much more soluble than the unsubstituted tetraphenylcyclobutadiene

TABLE 1

PRODUCTS AND YIELDS OBTAINED FROM REACTIONS OF ACETYLENES, RC_2R, WITH $(PhCN)_2PdCl_2$

R	Solvent	Yields[a] (%)		
		(II)	(III)	(IV)
C_6H_5	Benzene	34[b]	60	
C_6H_5	Diglyme	19[b]	55	
p-ClC_6H_5	Benzene	43[b]	32	
p-MeC_6H_4	Benzene	44[b]	39	
p-$MeOC_6H_4$	Benzene	58[b]	26	
C_6H_5	Ethanol			90
p-ClC_6H_5	Ethanol			66
p-MeC_6H_4	Ethanol			65
p-$MeOC_6H_4$	Ethanol	54[c]		

[a] Based on acetylene, [b] $n=3$ in complex (II). [c] $n=1.5$ in complex (II).

complexes (Va). This allowed osmometric molecular weight measurements to be performed; all the complexes were shown to be dimeric.

In ethanol the *endo*-ethoxytetra-*p*-tolylcyclobutenyl complex (IVc) was obtained in the same way as the other *endo*-ethoxycyclobutenyl complexes (IVa and b) (Table 1). However, di-*p*-anisylacetylene did not give this complex under any conditions; the only product which could be isolated was the cyclobutadiene complex, $[(p\text{-}MeOC_6H_4C)_4(PdCl_2)_{1.5}]_2$. It is reasonable to suppose that (IVd) is, however, still an intermediate but that ethoxide is readily removed from this intermediate owing to the presence of the strongly electron-donating *p*-anisyl groups on the ring. In contrast to the complexes (Va, b and c), which all reacted readily with ethanol to give the *exo*-ethoxycyclobutenyl complexes (VI), (Vd) was again inert. Under more vigorous conditions (NaOEt in ethanol) complete decomposition to metal and unidentified products occurred. This again implies that alkoxytetra-*p*-anisylcyclobutenyl complexes are very unstable with respect to (Vd). Attempts to prepare the $[(exo\text{-}EtOC_4R_4)NiX]_2$ from (IX) were also unsuccessful; reaction appeared to occur but no pure materials were isolable.

All the cyclobutadiene complexes (II) and (V) reacted with tert-phosphines to give the cyclooctatetraenes (VII)[3]. Tri-n-butylphosphine was the reagent of choice (though other phosphines and phosphites reacted with equal facility) since it gave the very soluble $(Bu_3P)_2PdX_2$, which was easily separated from the cyclooctatetraene. Yields are reasonably high and this represents a useful route for the synthesis of substituted cyclooctatetraenes.

The related ligand-exchange reactions, in which the complexes (Va–d) were reacted with $(Bu_3P)_2NiX_2$ to give $(Bu_3P)_2PdX_2$ and the cyclobutadiene–nickel complexes (IXa–d) in high yield have already been reported[5]. The complexes (IXa, c) were also prepared by ligand-transfer reactions in which the palladium complexes (Va, c) were treated with nickel carbonyl at ca. 40° in a variety of solvents.

When nickel carbonyl was added to a benzene suspension of (V) at 80°, very little of the cyclobutadiene–nickel complex was isolated. The major product under these conditions was the cyclopentadienone (VIII) obtained in better than 50% yield. Carbon monoxide itself did not react with (Va) except under high pressure and eleva-

TABLE 2

YIELDS AND ANALYTICAL DATA ON NEW COMPOUNDS PREPARED

Compound[a]	Yield (%)	M.p. (°C)	Prepared from	Found				Calc'd.			
				C(%)	H(%)	Other(%)	Mol. wt.	C(%)	H(%)	Other(%)	Mol. wt
To_6C_6 (IIIc)	39	subl. >320	(Ic)	93.05	7.01		619[c]	93.19	6.81		619
$[To_4C_4PdCl_2]_2$ (Vc)	90		(IIc)	65.16	4.78	Pd, 17.9	1180[d]	65.05	4.76	Pd, 17.7	1110
$[To_4C_4(PdCl_2)_3]_2$ (IIc)	44		(Ic)			Pd, 33.6				Pd, 33.6	
$[(To_4C_4OEt)PdCl]_2$ (IVc)	66	165–175[b]	(Ic)	67.92	5.43	Pd, 17.5	1160[d]	68.11	5.55	Pd, 17.8	1199
$[To_4C_4PdBr_2]_2$ (Vc)	61	>150[b]	(IVc)	56.74	3.98	Pd, 15.6	1280[d]	56.61	4.16	Pd, 15.7	1358
$[(To_4C_4OEt)PdCl]_2$ (VIc)	59	204–206[b]	(Vc)	66.23	5.33	Pd, 17.6	1150[d]	68.11	5.55	Pd, 17.8	1199
To_8C_8 (VIIc)	38	359-361	(IIc)	93.33	7.00		825[c]	93.19	6.81		825
$[To_4C_4]Fe(CO)_3$ (Xc)	47	229-230	(Vc)	76.23	5.06		552[c]	76.10	5.11		552
To_4C_4CO (VIIIc)	59	240-241	(Vc)	89.80	6.64		441[c]	89.95	6.41		441
$(To_4C_4PdC_5H_5)FeBr_4$ (XIIc)	56	>260[b]	(Vc)	46.53	3.66			46.31	3.47		
$(To_4C_4PdC_5H_5)Br$ (XIIc)	91	>130[b]	(XIIc)	66.89	5.22			67.00	5.03		
[*exo*-$MeOTo_4C_4PdC_5H_5$]	77		(XIIc)	74.15	5.76		614[c]	74.25	5.88		615
$[To_4C_4NiBr_2]_2$ (IXc)	73		(Vc)	60.89	4.43		1210[d]	60.90	4.47		1262
$(To_4C_4NiC_5H_5)FeBr_4$ (XIIIc)	89		(IXc)	48.58	3.60			48.80	3.67		
$(To_4C_4NiC_5H_5)Br$ (XIIIc)				72.32	5.51			72.10	5.40		
[*exo*-$MeOTo_4C_4NiC_5H_5$]	60		(XIIIc)	80.51	6.26		566[c]	80.50	6.38		567
$[An_4C_4(PdCl_2)_3]_2$ (IId)	59		(Id)			Pd, 31.8				Pd, 31.6	
$[An_4C_4PdCl_2]_2$ (Vd)	84		(IId)	58.72	4.37	Cl, 10.27 Pd, 16.3		58.78	4.31	Cl, 10.84 Pd, 16.1	
$[An_4C_4PdBr_2]_2$ (Vd)	78		(IId)			Pd, 15.7	1410[d]			Pd, 15.7	1485
An_6C_6 (IIId)	26	408–409	(Id)'	80.86	6.16		714[c]	80.67	5.93		714
An_8C_8 (VIId)	94	329-331	(IId)	80.50	6.00		953[c]	80.67	5.93		953
$[An_4C_4NiBr_2]_2$ (IXd)	77		(Vd)	54.87	4.50		1340[d]	54.97	4.26		1390
$An_4C_4Fe(CO)_3$ (Xd)	17	98-99.5	(Vd)	68.04	4.59	Fe, 9.78	616[c]	68.19	4.58	Fe, 9.06	616
$[An_4C_4PdC_5H_5]Br$ (XIId)	84					Pd, 14.6				Pd, 14.7	
$Ph_4C_4Ru(CO)_3$ (XIa)	42	218-219	(Va)	68.77	3.88		542[d]	68.75	3.75		542

[a] Ph=C_6H_5; To=*p*-MeC_6H_4; An=*p*-$MeOC_6H_4$. [b] With decomposition. [c] Mass-spectrometric molecular weight. [d] Osmometric molecular weight.

ted temperature when the product was the tetraphenyl-2-cyclopenten-1-one[6]. This difference in behavior is not understood, but it is apparent that in the reaction described here the nickel carbonyl also plays a role other than as a source of carbon monoxide.

Iron pentacarbonyl underwent ligand-transfer reactions with (V). In most cases the cyclobutadieneiron tricarbonyl complexes (Xa–d) were isolated in good yield. The nickel complex (IXa) similarly reacted with $Fe(CO)_5$ to afford (Xa) in 90% yield.

$$\underset{\text{(IXa)}}{[Ph_4C_4NiBr_2]_2} + Fe(CO)_5 \rightarrow \underset{\text{(Xa)}}{Ph_4C_4Fe(CO)_3}$$

The reverse reaction was also possible; (tetraphenylcyclobutadiene)iron tricarbonyl served in the preparation of the palladium chloride complex (IIa) by reaction with $(PhCN)_2PdCl_2$ in refluxing benzene.

$$\underset{\text{(Xa)}}{Ph_4C_4Fe(CO)_3} + (PhCN)_2PdCl_2 \xrightarrow[80°]{C_6H_6} \underset{\text{(IIa)}}{[Ph_4C_4(PdCl_2)_3]_2}$$

In one case we also observed a similar reaction with $PtCl_2$; however, the yield of the presumed $Ph_4C_4PtCl_2$ was too small for characterisation. Triruthenium dodecacarbonyl also reacted with (Va); higher temperatures (chlorobenzene at reflux) were needed here for complete conversion to (XIa). Uncharacterised intermediates were obtained at lower temperatures. The complex (XIa) has also been prepared by Sears and Stone[7].

The cyclopentadienylation by $C_5H_5Fe(CO)_2Br$ of both the nickel and palladium bromide complexes $[(p\text{-}MeC_6H_4C)_4MBr_2]_2$ was carried out. The *p*-tolyl analogs (XIIc) and (XIIIc) of the already described cyclopentadienyl(tetraphenylcyclobutadiene)nickel and -palladium cations[8] were obtained. These reacted with sodium methoxide in methanol to give the *exo*-methoxycyclobutenyl complexes.

$$[(p\text{-}MeC_6H_4)_4C_4MC_5H_5]Br + OMe^- \rightarrow exo\text{-}MeO(p\text{-}MeC_6H_4)_4C_4MC_5H_5$$

NMR SPECTRA

The ^1H NMR spectra of the complexes described have been measured and details are presented in Table 3. These spectra were of considerable help in proving the structures of the cyclobutadiene complexes. It was found that in all cases where other arguments suggested a symmetrically bonded cyclobutadiene ring, the protons on the *p*-substituted phenyl rings were seen as an AB quartet at 60 MHz. Coupling across the rings was not observed. In fact, none of the complexes possesses an overall fourfold axis of symmetry when the ligands on the other side of the metal are also considered, and we presume that the equivalence of the phenyl protons which was observed is due to rotation of the cyclobutadiene ring about its axis to the metal. Compounds in which the four *p*-substituted phenyls were not equivalent, including (IV), (VI) and (VIII), showed a complex multiplet in the phenyl region.

At higher resolution than was attainable, it may well also be possible to use the methyl resonances in *p*-tolyl complexes to test for symmetry. The *endo*-ethoxytetra-*p*-

TABLE 3

^{1}H NMR SPECTRA[a]

Complex[b]	Phenyl (δ)	J_{AB} (Hz)	p-Me, p-MeO (δ)	Other (δ)
$[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{PdBr}_2]_2$ (Vb)	7.7q	9.0		
$[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{NiBr}_2]_2$ (IXb)	7.6q	7.2		
$[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{PdC}_5\text{H}_5]\text{Br}$ (XIIb)	7.3q	8.4		C_5H_5 6.20
$\{[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{OEt}]\text{PdCl}\}_2$ (IVb)	7.3m			CH_2 3.5, CH_3 1.1
$\{[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{OEt}]\text{PdCl}\}_2$ (VIb)	7.4m			CH_2 3.7, CH_3 1.3
$(p\text{-ClC}_6\text{H}_4)_4\text{C}_5\text{O}$ (VIIIb)	7.1m			
$[\text{To}_4\text{C}_4\text{PdBr}_2]_2$ (Vc)	7.4q	9.0	2.28	
$[\text{To}_4\text{C}_4\text{NiBr}_2]_2$ (IXc)	7.5q	7.8	2.22	
$[\text{To}_4\text{C}_4\text{PdC}_5\text{H}_5]\text{Br}$ (XIIc)	7.5q	8.4	2.35	C_5H_5 6.05
$[\text{To}_4\text{C}_4\text{NiC}_5\text{H}_5]\text{Br}$ (XIIIc)	7.5q	8.4	2.36	C_5H_5 5.62
$\text{To}_4\text{C}_4\text{Fe(CO)}_3$ (Xc)	7.1q	7.8	2.27	
$[endo\text{-EtOTo}_4\text{C}_4\text{PdCl}]_2$ (IVc)	6.8m		2.10, 2.25, 2.45	CH_2 3.32 CH_3 0.91
$[exo\text{-EtOTo}_4\text{C}_4\text{PdCl}]_2$ (VIc)	7.5m		2.10, 2.35	CH_2 3.55, CH_3 1.03
$\text{To}_4\text{C}_5\text{O}$ (VIIIc)	7.5m		2.22	
$[\text{An}_4\text{C}_4\text{PdBr}_2]_2$ (Vd)	7.3q	9.0	3.81	
$[\text{An}_4\text{C}_4\text{NiBr}_2]_2$ (IXd)	7.4q	8.4	3.89	
$[\text{An}_4\text{C}_4\text{PdC}_5\text{H}_5]\text{Br}$ (XIId)	7.2q	9.0	3.92	C_5H_5 6.02

[a] 60 MHz, in $CDCl_3$. [b] To = p-MeC_6H_4, An = p-$MeOC_6H_4$.

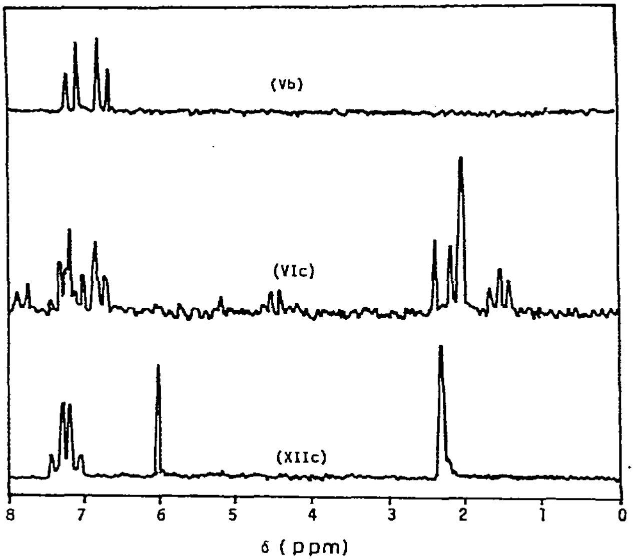


Fig. 1. ^{1}H NMR spectra of $[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{PdBr}_2]_2$, (Vb); $[endo\text{-EtO}(p\text{-CH}_3\text{C}_6\text{H}_4)_4\text{C}_4\text{PdCl}]_2$, (VIc) and $[(p\text{-CH}_3\text{C}_6\text{H}_4)_4\text{C}_4\text{PdC}_5\text{H}_5]\text{Br}$ (XIIc) in $CDCl_3$.

tolylcyclobutenyl complex (IVc) showed, as expected, three methyl resonances in the ratio of 1/1/2; however, in the *exo*-isomer (VIc) only two resonances of equal intensity could be resolved at 60 MHz.

Some examples of such spectra are shown in Fig. 1. We have previously also used similar spectra to show the presence of cyclobutadiene rings in some cobalt complexes[9]. The NMR spectra observed are all in agreement with the structures proposed here and previously[8].

EXPERIMENTAL

Di-*p*-tolylacetylene and di-*p*-anisylacetylene were prepared by the method of Coleman *et al.*[10]. Although most of the complexes were not air-sensitive, reactions were usually carried out under a nitrogen atmosphere. Analytical data are given in Table 2 and details of some representative reactions are given below. The syntheses of (XIIa) and (XIIIa) have been described elsewhere[9], and (XIIb, c) and (XIIIc) were prepared in the same manner. We are indebted to Dr. A. Efraty for experimental details of the complexes (XIIc), (XIIIc) and their reactions with methoxide.

(Tetra-p-tolylcyclobutadiene)palladium chloride $[To_4C_4PdCl_2]_2$ *(Vc) and Hexa-p-tolylbenzene (IIIc)*

A solution of 1.90 g (8.40 mmoles) of di-*p*-tolylacetylene (Ic) in 300 ml of benzene was slowly added over ca. 6 h to a well-stirred solution of 3.55 g (9.24 mmoles) of bis(benzonitrile)palladium chloride in 300 ml of benzene at 20°. The red precipitate formed was filtered off, and digested with two portions of 200 ml of hot benzene to remove hexa-*p*-tolylbenzene. Yield 1.90 g (44 %) of the brick-red complex, $[(p\text{-}MeC_6H_4C)_4(PdCl_2)_3]$, (IIc), after drying *in vacuo*.

The filtrate and washings were combined and the volume reduced to 50 ml *in vacuo*. The solution, which contained some benzonitrile and its palladium chloride complex, was poured through an alumina-filled chromatography column to remove these materials. Elution with benzene gave a colorless solution which, after evaporation to dryness and recrystallization, gave pure hexa-*p*-tolylbenzene (IIIc) (39 %). It sublimed in an evacuated capillary, beginning at 320°.

The complex (IIc) (1.0 g) was dissolved in 30 ml of dimethylformamide, filtered and poured into 150 ml of concentrated hydrochloric acid. The precipitate was collected on a filter, washed with water, dried and recrystallised from methylene chloride/petroleum ether to give 0.56 g (90 %) of red $[(p\text{-}MeC_6H_4C)_4PdCl_2]_2$, (Vc).

(Tetra-p-tolylcyclobutadiene)palladium bromide

The complex (IIc) (1.0 g) was suspended in 100 ml of methylene chloride and dry hydrogen bromide was bubbled through the suspension for 10 min. The resultant red solution was filtered, and the filtrate was taken to dryness on a rotary evaporator. The red solid was dissolved in methylene chloride and petroleum ether added to crystallise the dark red $[(p\text{-}MeC_6H_4C)_4PdBr_2]_2$. Yield, after filtration and drying, 0.29 g (40 %).

(endo-Ethoxytetra-p-tolylcyclobutenyl)palladium chloride dimer (IVc)

A solution of 0.78 g (2.0 mmoles) of bis(benzonitrile)palladium chloride in 50 ml of methylene chloride was added to a stirred suspension of 0.84 g (4.2 mmoles) of di-*p*-tolylacetylene in 100 ml of ethanol at 20°. The acetylene dissolved almost immediately and a yellow precipitate began to form shortly afterwards. This was filtered off after $2\frac{1}{2}$ h, and the precipitate washed with ethanol and dried. Yield of pure (*endo*-ethoxytetra-*p*-tolylcyclobutenyl)palladium chloride dimer, (IVc), 0.79 g (66%) after crystallization from methylene chloride/ethanol. This complex was also prepared in 90% yield, using sodium tetrachloropalladate in place of bis(benzonitrile)palladium chloride.

Dry hydrogen bromide was bubbled through a solution of 0.4 g of complex (IVc) in 50 ml of methylene chloride for 10 min. The color darkened, the solvent was removed and the residue recrystallised from methylene chloride/petroleum ether to give 0.27 g (61%) $[(p\text{-MeC}_6\text{H}_4\text{C})_4\text{PdBr}_2]_2$ identical to that prepared above.

(*exo-Ethoxytetra-p-cyclobutenyl*)*palladium chloride dimer*, (*VIc*)

A suspension of 0.5 g of the *p*-tolyl complex (Vc, X = Cl) in 100 ml of ethanol was stirred at 20° for 24 h. The solid now yellow, was filtered off and recrystallised from methylene chloride/petroleum ether. Yield 0.64 g (59%) of complex (VIc).

The *p*-anisyl complex (Vd) was recovered unchanged after stirring in ethanol for 48 h; reaction with sodium ethoxide in ethanol gave palladium metal.

Octa-p-tolylcyclooctatetraene (*VIIc*)

A suspension of 1.50 g (tetra-*p*-tolylcyclobutadiene)palladium bromide was refluxed in 150 ml of benzene for a few minutes. Tri-n-butylphosphine (1.0 g) was added; the reaction mixture turned green almost immediately and then slowly turned yellow. The reaction mixture was filtered and the solvent removed *in vacuo*, leaving an oil. The bis(tributylphosphine)palladium chloride was readily soluble in petroleum ether and was washed out of the residue, which, after crystallisation gave 0.44 g (40%) of octa-*p*-tolylcyclooctatetraene, (VIIc).

Tetra-p-tolylcyclopentadienone, (*VIIIc*)

A suspension of 0.50 g of (tetra-*p*-tolylcylobutadiene)palladium bromide (Vc) in 100 ml of benzene was refluxed for 5 min. Nickel carbonyl (4 ml) was added, the suspension darkened immediately and refluxing was continued for 2 h. Excess nickel carbonyl was blown off by a stream of nitrogen, the solution was filtered and reduced to low volume. This residue was chromatographed in alumina in benzene. The red band which eluted gave, after removal of the solvent and crystallization, 0.19 g (58%) of tetra-*p*-tolylcyclopentadienone (VIIIc).

When the above reaction was carried out as described but at a temperature of 40° after adding the nickel carbonyl, the main product was the rather insoluble (tetra-*p*-tolylcyclobutadiene)nickel bromide (IXc).

(*Tetraphenylcyclobutadiene*)*iron tricarbonyl* (*Xa*)

Freshly filtered iron pentacarbonyl (5 ml) was added to a suspension of 1.0 g of (tetraphenylcyclobutadiene)palladium bromide (Va) in 100 ml of benzene. The reaction mixture was refluxed with stirring for 2 h and then filtered to remove metal and evaporated to dryness. The residue which remained was dissolved in a minimum of benzene and chromatographed on alumina. (Tetraphenylcyclobutadiene)iron tricarbonyl was eluted first in benzene/petroleum ether (1/9 v/v) and was obtained in 0.62 g (78 %) yield as pale yellow crystals, m.p. 232° (lit. 234°[11]) after crystallisation from ethanol.

This complex was also synthesised in 90 % yield by an identical route from the nickel complex (IXa).

Reaction of (tetraphenylcyclobutadiene)iron tricarbonyl with bis(benzonitrile)palladium chloride to give (IIa)

A mixture of 0.45 g (0.91 mmole) of (tetraphenylcyclobutadiene)iron tricarbonyl and 1.80 g (4.70 mmole) of bis(benzonitrile) palladium chloride in 100 ml of benzene were refluxed together for 12 h and then filtered. The red-brown residue was washed with benzene, 7 % hydrochloric acid (to remove any iron salts) and then air-dried. This left 1.45 g (0.83 mmole) of $[Ph_4C_4(PdCl_2)_3]_2$ (IIa) (Found: Pd, 36.2. $C_{56}H_{40}Cl_{12}Pd_6$ calcd.: Pd, 35.9 %.) which was converted to $[Ph_4C_4PdBr_2]_2$ as described above.

(Tetraphenylcyclobutadiene)ruthenium tricarbonyl (XIa)

A mixture of 0.41 g (0.33 mmole) of (tetraphenylcyclobutadiene)palladium bromide and 0.42 g (0.66 mmole) of triruthenium dodecacarbonyl were refluxed with stirring in 50 ml of chlorobenzene for 12 h. The reaction mixture was filtered to remove metals and the solvent removed from the filtrate. The residue left was extracted with methylene chloride and petroleum ether added to the combined extracts to precipitate 0.15 g (42 %) of yellow (tetraphenylcyclobutadiene)ruthenium tricarbonyl, (XIa).

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