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SYNTHESES, SPECTROSCOPIC CHARACTERIZATION AND ELECTRONIC STRUCTURE OF CYCLOPROPENYLIDENE LIGATED PLATINUM COMPLEXES

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ABSTRACT

New series of platinum complexes of cyclopropenylidenes of the types of $PtX_2(CP)_2$ and *trans*-$PtX(PBu_3)_2(CP)$ have been synthesized, where CP is di-*t*-butylcyclopropenylidene (BCP) or bis(diisopropylamino)cyclopropenylidene (ACP). The ^{13}C-NMR chemical shifts, and ^{13}C–^{195}Pt coupling constants ($^1J_{PtC}$) for the complexes are discussed in comparison with those values derived from closely related series of compounds, *trans*-$PtCl(PR_3)_2L$; L = —CH_3, —C_6H_5 and —C≡CBu-*t*. An excellent linear relationship through the origin was obtained between $^1J_{PtC}$ and the formal '*s*' % character of the carbon directly bonded to Pt for the series *trans*-$PtCl(PR_3)_2L$ in which the Pt—C bond is regarded as a pure σ-linkage, whereas $^1J_{PtC}$ deviates largely from this relationship when pπ—dπ bonding interaction possibly exists in the Pt—C bond. The NMR data suggest the strong nmr *trans*-influence of the cyclopropenylidenes and that in the Pt—CP bond the σ-interaction is appreciable but the π-interaction is negligible.

INTRODUCTION

Since the structural novelty of cyclopropenylidene was pointed out,[1a] this carbene species and its derivatives have been attracting much attention from theoretical[1] and experimental[2] chemists. Study on the carbene ligating to metals is also intriguing, and we have been continuing with synthesis and structural investigation of novel cyclopropenylidene metal complexes.[2f,3c–f]

In addition to such interest in structural chemistry, our recent interest has been directed toward the characteristic nature of cyclopropenylidene derivatives as ligands. That is, in contrast to usual electrically neutral Lewis-base ligands such as PR_3, AsR_3, SR_2, NR_3 and CO, the carbene species are essentially undissociative when they form complexes with certain transition metals. As pointed out by Clark *et al.*[4] if we could systematically change one ligand, L′, of a low symmetry species of the type $MLL'X_2$ (L and L′: neutral ligand), it would be extremely useful for investigating a reaction involving transition metal complexes, such as intramolecular rearrangements, catalytic behaviors, etc.. However, these species containing monodentate ligands have a tendency to disproportionate to more symmetric complexes. The

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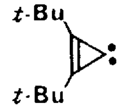
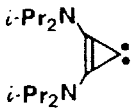
undissociative nature of cyclopropenylidene derivatives might offer a possibility to obtain stable metal complexes of low symmetry. [2d] In fact, a mechanism of metal complex catalyzed cycloreversion of quadricyclane has been elucidated[5] by using $PdCl_2(CP)L$ (CP = substituted cyclopropenylidene, L = 4-substituted pyridine).

In the course of our study of such a problem, it has become necessary to know the electronic nature of the cyclopropenylidene—metal bonding; magnitude of *trans*-influence, pπ—dπ bonding, hybridization of the ligating carbon, σ—π conjugative effect and so forth. However, little was known about the electronic nature of the bonding between metals and cyclopropenylidenes.

We have selected di-*t*-butylcyclopropenylidene (BCP) and bis(diisopropylamino)cyclopropenylidene (ACP) as the ligands, because they are largely different in the nature of their π-systems, due to the large difference betwen the *t*-butyl group and the amino group in π-donating ability. That is, the p-type orbital on the carbene carbon is raised much higher in energy in ACP than in BCP by mixing with their ethylenic π–moieties.[1k] Consequently, valuable information for π-type bonding in M-carbene could be obtained by comparing BCP-M and ACP-M.



BCP



ACP

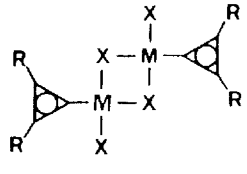
NMR parameters might offer us useful information for the electronic structure of the complexes. Thus, our attention was directed toward cyclopropenylidene platinum complexes, because the naturally occurring magnetic isotope (^{195}Pt, 34%) allows us to obtain abundant NMR parameters including ^{195}Pt–^{13}C coupling constants $^1J_{PtC}$.

We now wish to report (1) a study of the synthesis of novel cyclopropenylidene platinum complexes, (2) ^{13}C- and ^{195}Pt-NMR characterization of cyclopropenylidene platinum complexes, and (3) electronic structure of the platinum—cyclopropenylidene bond.

RESULTS AND DISCUSSION

Syntheses of cyclopropenylidene platinum complexes

We have reported[3d,e] the preparation of Pd^{II} complexes including $Pd_2Cl_4(BCP)_2$ (**1**) and $Pd_2Cl_4(ACP)_2$ (**2**) by the oxidative addition reaction of Pd^0 with the corresponding dichlorocyclopropenes.

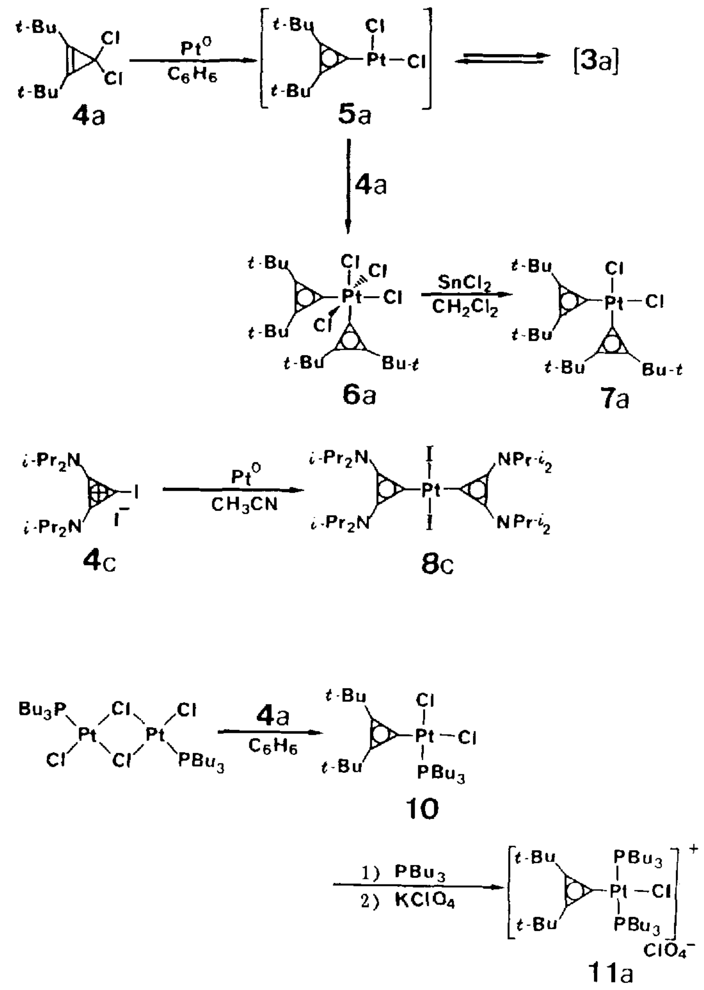


1 ; $M = Pd^{II}$, $R = t\text{-Bu}$, $X = Cl$
2 ; $M = Pd^{II}$, $R = i\text{-}Pr_2N$, $X = Cl$
3a ; $M = Pt^{II}$, $R = t\text{-Bu}$, $X = Cl$
3b ; $M = Pt^{II}$, $R = i\text{-}Pr_2N$, $X = Cl$
3c ; $M = Pt^{II}$, $R = i\text{-}Pr_2N$, $X = I$

In the present study the reactions of Pt^0 (platinum black) with dichlorocyclopropenes have been examined. As shown in Scheme 1, when di-*t*-butyldichlorocyclopropene (**4a**) was treated with Pt^0 in a manner similar to the preparation of **1**, the cyclopropenylidene platinum complex obtained was bis(di-*t*-butylcyclopropenylidene)tetrachloroplatinum (**6a**) instead of the anticipated binuclear complex $Pt_2Cl_4(BCP)_2$ (**3a**). The Pt^{IV} complex $PtCl_4(BCP)_2$ (**6a**) should be formed by further oxidative addition of **4a** to initially formed cyclopropenylidenedichloroplatinum, $Pt^{II}Cl_2(BCP)$ (**5a**). The Pt^{IV} complex, **6a**, can be easily reduced to the Pt^{II} complex, $PtCl_2(BCP)_2$ (**7a**), by treatment with 1 equiv. of $SnCl_2$ in CH_2Cl_2. Their stereochemistry of *cis*-configurations was determined based on the ^{195}Pt–^{13}C coupling constants, 1040 Hz and 1438 Hz, for **6a** and **7a**, respectively (*vide infra*).

Treatment of bis(diisopropylamino)chlorocyclopropenium chloride (**4b**) with Pt^0 in a similar manner has resulted in recovering the starting materials. When iodo derivative **4c** was employed, *trans*-$PtI_2(ACP)_2$ (**8c**) was obtained together with di-μ-iodide complex **3c**. The plausible reaction mechanism for the formation of **8c** might involve the oxidative addition of the two molecules of **4c** with Pt^0 leading to $Pt^{IV}I_4(ACP)_2$ (**6c**) followed by the reductive elimination of I_2 from **6c**.

Scheme 1

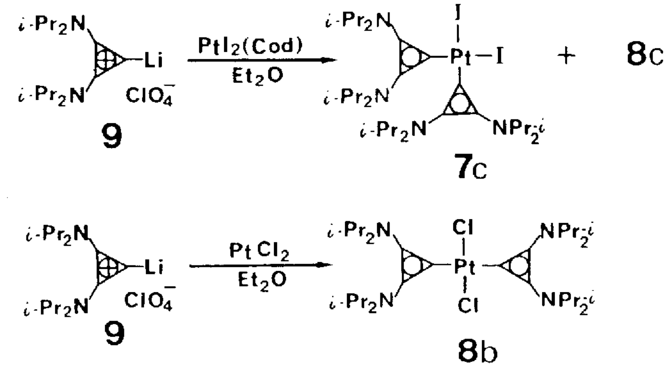


The *cis*-counterpart of **8c** was obtained by the ligand exchange reaction using bis(diisopropylamino)lithiocyclopropenium perchlorate (**9**).[2f,3d] Thus, treatment of $PtI_2(COD)$ with **9** in ether at −5–0 °C afforded a mixture of **7c** and **8c** (Scheme 2). The product ratio **7c**/**8c** was unsteady, and in some cases **8c** was obtained predominantly and only a trace of **7c** was detected. They were separated by TLC (silica gel, CH_2Cl_2/Ether = 50/1) at low temperature (below −5 °C). The complex **7c** gradually isomerized to **8c**. Although the isomers cannot be distinguished by their IR finger print region absorptions, their FIR spectra exhibit a marked distinction. In the Pt–I frequency region in the FIR,[6] **8c** gave a band at 193 cm^{-1} whereas **7c** gave a signal for ν_{PtI} at 134 cm^{-1}. Since the *trans*-influence of ACP would be much larger than that of I^-,[3f] the lower value of ν_{PtI} for **7c** than for **8c** indicates the *cis*- and *trans*-configurations for **7c** and **8c**, respectively.

Treatment of **9** with $PtCl_2(COD)$ was unsuccessful because $PtCl_2(COD)$ did not react with **9** and was recovered. Although yield was poor, **8b** was obtained by the reaction of **9** with $PtCl_2$ in ether (Scheme 2). The high Pt—Cl stretching frequency, 324 cm^{-1}, in the FIR of **8b** indicates the mutual *trans*-orientation of chlorine atoms.[7] No trace of *cis*-$PtCl_2(ACP)_2$ could be detected in the reaction mixture.

One of the I^- ions in **8c** was replaced by Cl^- to afford $PtClI(ACP)_2$ (**8d**) by treating **8c** with CF_3SO_3Ag in CH_2Cl_2/CH_3CN and successive addition of Et_4NCl.

Scheme 2



In order to examine a series of closely related platinum complexes possessing a variety of σ-linked carbon ligands, we have selected the *trans*-$PtCl(PR_3)_2L$ type complexes (L = carbon ligand), since there have been systematic NMR studies for this type of complex.[8] Also, fortunately, *trans*-$[PtCl(PR_3)_2(ACP)]^+ClO_4^-$ (**11b**) can be easily prepared by the reaction of *trans*-$PtCl_2(PR_3)_2$ with **9**.[3d]

As shown in Scheme 1, in the reaction of Pt^0 with **4a** the plausible intermediate should be $Pt^{II}Cl_2(BCP)$ (**5a**). This scheme has inspired us to examine a reaction of **4a** with a species of the type $Pt^{II}Cl_2L$ (L = neutral ligand) to obtain a mono BCP platinum complex. PBu_3 was selected as L, and since $Pt^{II}LCl_2$ should exist in equilibrium with the corresponding di-μ-chlorodimer $Pt_2Cl_4L_2$, **4a** was treated with $Pt_2Cl_4(PBu_3)_2$ in benzene under reflux. The reaction gave *cis*-$PtCl_2$ (PBu_3) (BCP) (**10**) in 22% yield (Scheme 1). Treatment of **10** with 1 equiv. of PBu_3 afforded *trans*-$[PtCl(PBu_3)_2(BCP)]^+Cl^-$ in quantitative yield.

A series of complexes of the type *trans*-$PtCl(PBu_3)_2L$, L = $C_6H_5^-$ (**14b**), L = CH_3^- (**15b**) and L = *t*-BuC≡C$^-$ (**12a**), were synthesized according to the literature[9] appropriate for the preparation of each complex (see Experimental Section).

The ^{13}C- and ^{195}Pt-NMR and the spectroscopic characterization of BCP- and ACP-ligated Pt complexes

^{13}C-NMR. ^{13}C-NMR chemical shifts for the carbon (represented as C_1 hereinafter) directly bonded to Pt and the carbons (represented as C_2) next to C_1 are shown in Table 1 for the complexes studied in this work. Absolute values of ^{13}C–^{195}Pt coupling constants ($^1J_{PtC}$) and two bond ^{31}P—Pt—$^{13}C_1$ coupling constants ($^2J_{PPtC}$) are also tabulated (Table 1).

In all cases except **14b** and **15b** in Table 1, the measurements of ^{13}C-NMR suffered from poor nmr sensitivity of C_1, presumably due to long relaxation time. For example, the ^{195}Pt-satellites for C_1 of **11b** were barely observed using a NMR spectrometer operating at a ^{13}C-resonance frequency of 100·4 MHz employing pulse repetition intervals of 100 sec. In the case of **12a**, ^{195} Pt-satellites for the acetylide carbon could not be observed even employing pulse repetition intervals of 300 sec with a sample of very high concentration (*ca.* 40 wt %).

In each of the ^{13}C-NMR spectra of the Pt complexes in Table 1 except **12**, C_1 gave a resonance flanked by two ^{195}Pt-satellites. Each of the components (a central resonance and two ^{195}Pt-satellites) for C_1 of the complexes of the type *trans*-$PtCl(PBu_3)_2L$ appears as a triplet due to coupling with the two equivalent phosphorus nuclei, indicating the *trans*-orientation of two PBu_3.

It is well known that $^1J_{PtC}$ magnitude is sensitive to the nature of the ligand *trans* to C_1 and nmr *cis*-influence is small.[7] The $^1J_{PtC}$ values for **8b,c,d** spanning 935–986 Hz are much smaller than 1374 Hz for **11b**, indicating that the nmr *trans*-influence of the ligand *trans* to ACP in **8** is much higher than Cl^- which is *trans* to ACP in **11b**. This is consistent with the *trans*-configuration of **8b,c** deduced by Pt—halogen stretching frequencies (*vide supra*). The large ^1JPtC value, 1438 Hz, for **7a** comparable to 1369 Hz for **11a** indicates that the nmr *trans*-influence of the ligand *trans* to BCP in **7a** is as small as that of Cl^- which is *trans* to BCP in **11a**. This is consistent with the *cis*-configuration of **7a**. Similarly the $^1J_{PtC}$, 1400 Hz, for **10** also indicates its *cis*-configuration.

^{195}Pt-NMR. ^{195}Pt-NMR parameters are also summarized in Table 1. The ^{195} Pt-resonance appeared as a singlet for **6**, **7** and **8**, as a triplet for the complexes of the type *trans*-$PtCl(PBu_3)_2L$, and as a doublet for **10**. In all cases except **6a**, ^{195}Pt-resonance appeared in the chemical shift region -3300 ppm $\sim$ -4500 ppm typical for Pt^{II} square planar complexes.[10] The ^{195}Pt-NMR spectrum of **6a** showed a singlet at -717 ppm in the chemical shift region for Pt^{IV} complexes.[11]

In the case where the measurement of the ^{195}Pt-satellites of ^{13}C-NMR of C_1 is difficult owing to a long relaxation time of the carbon, ^{195}Pt-NMR is a potent alternative to obtain $^1J_{PtC}$, because ^{195}Pt-NMR should be accompanied by ^{13}C-satellites due to the $^{13}C_1$ isotopomer. Here we have measured ^{13}C-satellites of ^{195}Pt-NMR due to the ^{13}C-isotopomer of natural abundance (1·1%). For this purpose the measurements were performed on samples of high concentration (*ca.* 0·15 M), and FID signals were accumulated until a ^{195}Pt-signal/noise ratio over 200 was obtained. Each resonance of ^{195}Pt triplet for **14b** is flanked by the small ^{13}C-satellites, and the separation of the satellites (984 Hz) was independent of the NMR operating parameters. This was also the case for **8b** and **11b**. In all cases, the center of ^{13}C-satellites, which is the ^{195}Pt-chemical shift δ Pt for $^{13}C_1$-isotopomer, is *ca.* 0·6 ppm higher than that for $^{12}C_1$-counterpart. A similar isotope shift in ^{195}Pt-NMR was observed by Heaton and his co-workers in their ^{195} Pt-NMR study[12] on ^{13}C-enriched $Pt(CN)_4^{2-}$.

As shown in Table 1, the $^1J_{PtC}$ thus determined are essentially identical with the values

Table 1. ^{13}C- and ^{195}Pt-NMR parameters for the cyclopropenylidene platinum and related complexes[a]

	Complexes[b]	^{13}C-NMR of the Carbon Ligands[c]				^{195}Pt-NMR[e]		
		C_1 ppm	C_2 ppm	$^{1}J_{PtC}$[d] Hz	$^{2}J_{PPtC}$ Hz	Pt ppm	$^{1}J_{CPt}$[f] Hz	$^{1}J_{PtP}$ Hz
6a	*cis*-$PtCl_4$ $(BCP)_2$	166·6	195·3	1040 (2)		*−715		
7a	*cis*-$PtCl_2$ $(BCP)_2$	*178·2	*192·4	*1438 (2)		*−3315		
7c	*cis*-PtI_2 $(ACP)_2$	[g]	[g]	[g]		−3922	[g]	
8b	*trans*-$PtCl_2$ $(ACP)_2$	136.0	146·7	986 (2)		−3150	984 (5)	
8c	*trans*-PtI_2 $(ACP)_2$	*131·8	*146·6	*935 (2)		−4718		
8d	*trans*-PtICl $(ACP)_2$	134·6	146·9	956 (2)		*−3928		
10	*cis*-$PtCl_2$ (PBu_3) (BCP)	184·8	192·6	1400 (2)				3603 (5)
11a	*trans*-PtCl $(PBu_3)_2$ (BCP)	184·7	195·0	1369 (2)	9 (2)	*−4236		*2250 (5)
11b	*trans*-PtCl $(PBu_3)_2$ (ACP)	110·3[i]	143.8[i]	1374 (5)	11 (2)	−4321[i]	1369 (5)[i]	2344 (5)
12a	*trans*-$PtCl(PBu_3)_2$ (C≡CBu-t)	*63·0	*107·1	[g]	*15 (2)	*−4453	*1413 (5)	*2419 (5)
12b	*trans*-PtCl $(PBu_3)_2$ (C≡CPh)					*−4436[h]		*2373 (5)[h]
14b	*trans*-PtCl $(PBu_3)_2$ (C_6H_5)	138·3	137·6	935 (2)	9 (2)	−4267[i]	937 (5)[i]	2774 (5)
						−4267	937 (5)	2771 (5)
15b	*trans*-PtCl $(PBu_3)_2$ CH_3	* -24·3		*694 (2)	*7 (2)	*−4482		*2795 (5)

[a] Recorded on a JEOL JNM-FX90Q spectrometer operating at 22·5 MHz for ^{13}C- and ^{195}Pt, respectively, unless otherwise noted. Spectra were measured in CD_2Cl_2 solution other than starred values recorded in $CDCl_3$. Values in parentheses denote experimental error limit.

[b] **11a** and **11b** were in their ClO_4^- salts.

[c] Chemical shifts are reported in δ ppm (±0·1) from TMS. C_1 denotes the carbon directly bonded to Pt and C_2 symbolyzes the carbon next to the C_1.

[f] Determined based on ^{13}C-satellites in ^{195}Pt-NMR.

[g] Could not be observed. See text.

[h] Z. Yoshida, T. Ohno, H. Terao and S. Miki. The 32th Symposium on Coordination Chemistry, Sendai Japan, 1981, Preprint p. 64.

[i] Recorded on a JEOL JNM-GX 400 operating at 100·1 MHz and 85.5 MHz for ^{13}C- and ^{195}Pt NMR, respectively.

[h] Z. Yoshida, T. Ohno, H. Terao and S. Miki. The 32th Symposium on Coordination Chemistry, Sendai Japan, 1981, Preprint p. 64.

[i] Recorded on a JEOL JNM-GX 400 operating at 100·1 MHz and 85.5 MHz for ^{13}C- and ^{195}Pt NMR, respectively.

obtained from ^{195}Pt-satellites in ^{13}C-NMR, confirming the validity of the technical approach to get ^{13}C-^{195}Pt coupling constants. By this method $^{1}J_{PtC}$ for **12a** was determined to be 1413 Hz.

^{13}C-Shieldings. In each of the BCP and the ACP series in Table 1, the chemical shifts for C_2 reveals little alteration, in contrast to a large alteration of the ^{13}C-shielding of C_1. In the case of the ACP series, for example, the chemical shift of C_1 varies from 131·8 ppm to 110·3 ppm spanning 21·5 ppm, whereas the chemical shifts of C_2 reveal little change, from 143·8 ppm to 146·9 ppm. The chemical shift behavior is similar to the case of phenyl ring carbons in $PtL(C_6H_5)(AsMe_3)_2$ reported by Clark and Ward,[8b] and in direct analogy with their discussion, only minor changes in Pt-C_1 bond (at least the π component) may occur throughout each of BCP and ACP series. The carbene carbon of **11b** is much more shielded than the C_1 of **8**. This phenomenon is comparable to the similar observations that the more carbene is deshielded, the greater the *trans*-influence of the ligand *trans* to the carbene.[8a]

Comparison of the ^{13}C-NMR of the ring carbons of **11a** and **11b** showed that the marked upfield shifts of ^{13}C-NMR for both of C_1 and C_2 were caused by replacing *t*-butyl groups with N(*i*-Pr)$_2$ groups suggesting considerable π electron releasing from the NR_2 into the C_3 core.

Figure 1 shows the ^{13}C chemical shifts of the ring carbons of **11** and the corresponding methylcyclopropenium ions **16a** and **16b**. The C_2 carbons of **11** are deshielded in comparison with the corresponding carbons of **16** by $\Delta\delta(C_2)_a = 12{\cdot}5$ ppm and $\Delta\delta(C_2)_b = 10{\cdot}2$ ppm for **11a**–**16a** and **11b**–**16b**, respectively. Since deshielding neighboring anisotropic effect of the platinum moiety should operate on C_2,[8] the difference $\Delta\delta(C_2)$ is not the net result of the difference between the methyl and the $PtCl(PBu_3)_2$ groups in their through bond substituent effects on C_2.

Comparison of the differences, $\Delta\delta(C_2)_a$ and $\Delta\delta(C_2)_b$, would be informative. The difference of differences, $\Delta\Delta\delta(C_2) = \Delta\delta(C_2)_a - \Delta\delta(C_2)_b$, might be a measure of the difference of sensitivity between BCP and ACP to respond to the replacement of the methyl group by the platinum group. Since the neighboring anisotropic effect of the platinum group on C_2 is considered to be similar in **11a** and **11b**, the anisotropy term might be cancelled out and the net result of through bond substituent effect might dominantly reflect onto the $\Delta\Delta\delta(C_2)$ value. The ACP moiety should be much less sensitive to the π-donating substituent effect than BCP, because of the increased stabilization achieved by π donation from NR_2 into the C_3 core. In contrast to the ACP ring, BCP could be a good π acceptor. Therefore, we would anticipate larger $\Delta\Delta\delta(C_2)$, if there was a significant difference in π donating property between methyl group and $PtCl(PBu_3)_2$ group. It seems likely that the absolute magnitude of d—π^* interaction in the Pt-cyclopropenylidene bonds is as small as the π type interaction between methyl groups and the C_3^+ core in **16a** and **16b**.

^{13}C-^{195}Pt coupling constants. It is now well realized that Fermi contact interaction between the nuclear spin and the *s*-electrons at the nucleus dominantly contributes to ^{13}C-^{195}Pt coupling constants ($^{1}J_{PtC}$), and consequently the magnitude is sensitive mainly to the hybridization of the bonding orbitals between these atoms.[10,13]

The dependency of $^{1}J_{PtC}$ on the contribution of carbon 2*s* orbital to the Pt—C bond has been examined by several groups.[8] Comparing a closely related series, *trans*-$PtCl(AsMe_3)_2R$, Clark and his co-workers demonstrated the correlation of $^{1}J_{PtC}$ with the '*s*' character of the Pt—C at the carbon.[8a] They reported ^{1}J = 643 Hz for **15a** (R = CH_3: 25% '*s*'), 858 Hz for **14a** (R = C_6H_5: 33·3% '*s*') and 1724 Hz for **13a** (R = CO: 50% '*s*'). Although the gross change in

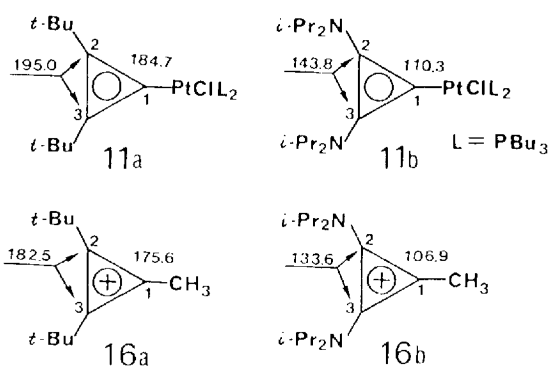


Figure 1. ^{13}C-NMR chemical shifts (δ, ppm) of the ring carbons of **11a**, **11b**, **16a** and **16b** as their ClO_4 salts

${}^1J_{PtC}$ in the series results from rehybridization, the interrelationship seems not to be so straightforward as the case of ${}^{13}C$–${}^1H$ coupling constants.

However, omitting **13a**, the ${}^1J_{PtC}$ varies in proportion to the formal '*s*' % character of the carbon σ-orbitals as shown in Figure 2 by the broken line, with filled circles for the *arsine* series. In our present work, a new *t*-butylethynyl complex (**12a**) was also prepared and the ${}^1J_{PtC}$ for **12a** was determined. Table 2 summarizes ${}^1J_{PtC}$ for Pt complexes having Cl^- as the common ligand *trans* to the carbon ligands. We have chosen PBu_3 as *cis*-ligands so that the cyclopropenylidene complexes of current interest can be included in the *phosphine* series.

Table 2. ^{13}C-chemical shifts and coupling constants for the complexes *trans*-$PtRClL_2$

	Complexes R	L	C_1 ppm	${}^1J_{PtC}$ Hz[a]	ref.	solvent
15a	CH_3	$AsMe_3$	−28·4	643 (2)	f	$(CD_3)_2CO$
14a	C_6H_5	$AsMe_3$	131·9	858 (1)	g	$CDCl_3$
13a[b]	CO	$AsMe_3$	159·2	1747 (3)	h	CD_2Cl_2
20[c]	CO	$AsPh_3$	158·2	1724	i	$CDCl_3$
15b	CH_3	PBu_3	−24·3	694 (2)	this work	$CDCl_3$
15c	CH_3	PMe_2Ph	−18·7	673 (3)	j	CD_2Cl_2
14b	C_6H_5	PBu_3	138·3	935 (2)	this work	CD_2Cl_2
12	t-BuC≡C	PBu_3	63·0	1413 (5)	this work	$CDCl_3$
13b[c]	CO	PPh_3	158·6	1788	i	$CDCl_3$
11a[d]	BCP	PBu_3	184·7	1369 (2)	this work	CD_2Cl_2
11b[d]	ACP	PBu_3	110·3	1374 (5)[e]	this work	CD_2Cl_2
16a[b]	:CMe (NMe_2)	$AsMe_3$	210·3	1070 (3)	h	$(CD_3)_2CO$

[a] Values in parentheses denote excrimental error limits.
[b] PF_6^- salt.
[c] BF_4 salt.
[d] ClO_4 salts; BCP denotes di-*t*-butylcyclopropenylidene; ACP denotes bis(diisopropylamino)cyclopropenylidene.
[e] Obtained by ^{13}C-satellites of ^{195}Pt-NMR.
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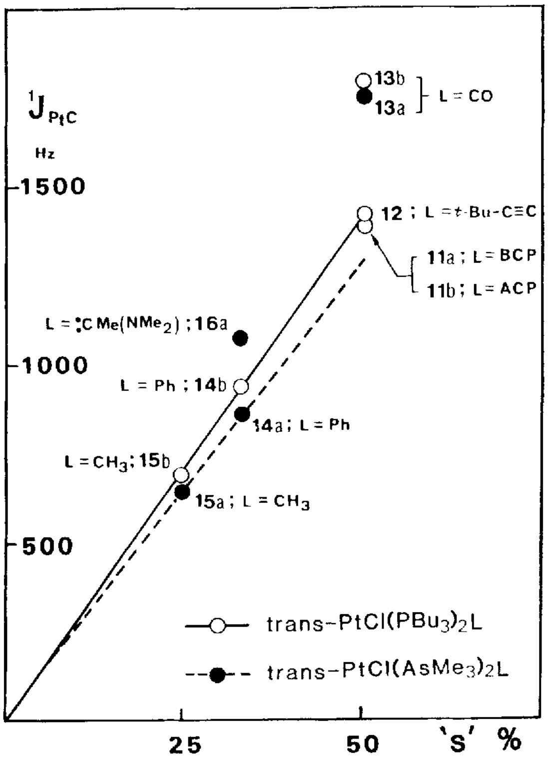


Figure 2. Plots of $^1J_{PtC}$ vs. '*s*' % character of the ligating σ-hybrid orbital of carbon ligand estimated based on formal hybridization

As is demonstrated by the solid line and open circles in Figure 2, the $^1J_{PtC}$ for **12a**, **14b** and **15b** varies in proportion to the '*s*' % of the carbon σ-orbital. The $^1J_{PtC}$ (673 Hz) for $PtCl(PMe_2Ph)_2CH_3$ (**15c**) reported[8a] matches the correlation also. The anomalous behavior of the CO complex can be observed also in the case of *phosphine* series. It seems likely that the $^1J_{PtC}$ values for the Pt—CO complexes deviate from the linear relationship for some reason(s) which does (do) not operate in the case of R = CH_3^-, $C_6H_5^-$ and *t*-BuC≡C$^-$.

The relationship obtained, equation (1), can be explained in terms of the appropriate form of the treatment of coupling constants by Pople and Santry, equation (2),[11]

$$^1J_{PtC}\ (\text{obsd.}) = 28{\cdot}03 \times \text{'}s\text{'} \tag{1}$$

$$^1J_{PtC} \propto \gamma_{Pt}\gamma_C\alpha^2_{Pt}\alpha^2_C|\psi_{Pt(6s)}(0)|^2|\psi_{C(2s)}(0)|^2(\Delta E)^{-1} \tag{2}$$

where γ is the magnetogyric ratio of the nucleus; α^2 is the '*s-character*' of the hybrid orbital; $|\psi_{X(ns)}(0)|^2$ is the valence *s*-electron density at the nucleus; and ΔE is an average excitation energy. Comparing the empirical relation, equation (1), with the theoretical equation (2), it can be inferred that ΔE, α^2_{Pt} and $|\psi_{X(ns)}(0)|^2$ change relatively little and the change in α^2_C should be the main factor to change the ^1J.

It thus appears that $^1J_{PtC}$ provides direct information about the carbon 2*s* contribution to the Pt—C_1 bond, if the comparison is performed for closely related complexes in which the Pt—C_1 bond can be regarded as a pure σ linkage.[14] However, in case the π interaction contributes to the metal—carbon bonding, the effect of the π component, if any, should be taken into account in interpreting individual $^1J_{PtC}$ values.

Thus, detailed discussion on the Pt—cyclopropenylidene bond should be preceded by examining the possibility for the π component to influence $^1J_{PtC}$ values. Although it is now well accepted that a non-Fermi contact mechanism such as π transmission[15] is negligible,[7] there are two possible ways by which π type bonding interaction could give variation to ^1J values. (a) As the Pt—C bond length is decreased by the pπ—dπ bonding interaction, [16] a synergic increase of σ—Pt—C bonding interaction would enhance $\alpha^2_{Pt}|\psi_{Pt(6s)}(0)|^2$ in equation (2). (b) Removal of charge from the metal *d*-orbital(s) through π back-bonding might increase $|\psi_{Pt(6s)}(0)|^2$ due to the increase of an effective atomic charge on 6*s* orbital. The former mechanism has been employed by Grim and his co-workers[17] to interpret the variation of $^1J(^{31}P—^{183}W)$ in changing electronegativity of R_3P in $R_3PW(CO)_5$. The latter has been indicated by Appleton, Clark and Manzer in their review, [7] referring to the relevant discussion of center shift in Mössbauer spectroscopy, which depends on *s*-electron density at the nucleus.[18]

Metal carbene complexes offer good empiricism for the argument, since metal—carbene bonds are written by a resonance structure (Figure 3), in which π bonding of the type of pπ—dπ is synergic with σ component.[19]

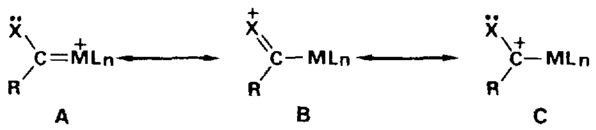
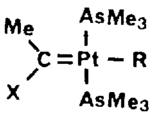


Figure 3. Possible resonance structures in a metal carbene complex

The $^1J_{PtC}$ value for *trans*-$PtCl(AsMe_3)_2(:CMeNMe_2)$ **18a** has been determined to be 1070 Hz.[8a] Since the plausible hybridization of the σ-bonding at the carbene carbon is sp^2, the observed value (1070 Hz) is much larger than the estimated $^1J_{PtC}$ value (860 Hz) for sp^2 carbon for the *arsine* series (Figure 2). The large discrepancy should be explained in terms of the π bonding interaction depicted by **A** in Figure 3 based on the mechanism (a) and/or (b).

It has been described that in the series of *trans*-$[PtMe(AsMe_3)_2(:CXMe)]^+PF_6^-$, $^1J_{PtC}$ decreases in the order X = OMe (**17b**, ^1J = 759 Hz) > X = NMe_2 (**18b**, ^1J = 694 Hz).[8a] Because of the strong π electron-donating nature of N atom compared with that of O atom, the resonance form **B** is more significant in **18b** than in **17b**, i.e. the resonance form **A** is less significant in **18b** than **17b**. Thus, the trend of $^1J_{PtC}$, **17b** >**18b**, is also attributable to the difference in the π bonding interaction.



17a : R = Cl, X = OMe
17b : R = Me, X = OMe
18a : R = Cl, X = NMe_2
18b : R = Me, X = NMe_2

The coupling constants ($^1J_{PtC}$) for **17b** and **18b** increase in the order **17b** (360 Hz) < **18b** (385 Hz), and this trend indicates the difference in magnitude of π bonding interaction. Since the π bonding interaction is stronger in **17b** than **18b**, the σ component should synergically increase in the order **17b** > **18b**. Any strengthening of the bond occurs at the expense of the Pt—L bond *trans* to the carbene carbon[20] resulting in the *trans*-influence order of :C(OMe)Me > :C(NMe$_2$)Me. Among the carbon ligands, CH_3^-, $C_6H_5^-$, *t*-BuC≡C$^-$, and CO in Table 2, Co is conspicuous in its tendency to make strong π bonding between transition metals. Therefore, it seems reasonable to attempt to explain the anomalies of $^1J_{PtCO}$ for **13a** and **13b** in terms of the π back-bonding interaction.

As mentioned above, there are many indications that the π bonding interaction between Pt and carbon ligands increases $^1J_{PtC}$ values. Therefore, the effect of d—π* on ^1J value must be taken into account in the interpretation of the coupling constant when a carbon ligand possesses low-lying π* orbital(s). Cyclopropenylidene platinum complexes are such cases, since σ—π synergic bondings can be considered for the Pt—cyclopropenylidene bond.

However, no anomalies were observed for $^1J_{PtC}$ for **11a** and **11b**. A linear relationship between $^1J_{PtC}$ and '*s*' % character (Figure 2) affords 49% '*s*' character of the ligating σ-orbital of carbene carbons for **11a** and **11b**. The result is in good agreement with the argument that the *exo* σ-orbitals of a cyclopropenium ring carbon possess *sp* configuration.[21] Consequently, it can be deduced that the absolute magnitude of the Pt—cyclopropenylidene π interaction may be negligible.

There might be another interpretation for the $^1J_{PtC}$ values for **11**. That is, the hybridization of the *exo* σ-orbital of cyclopropenylidene is less than *sp* in '*s*' character and π bonding interaction of considerable magnitude enhances the $^1J_{PtC}$ to afford the observed values. However this explanation seems unlikely because of the following reason. Since ACP would be much less likely than BCP to form π bonding, the order of $^1J_{PtC}$ of Pt—BCP > Pt—ACP should be anticipated, which immediately contradicts the fact that **11a** and **11b** reveal essentially identical values of $^1J_{PtC}$.

As is well known, $^1J_{PtC}$ magnitude is sensitive also to the hybridization of Pt—C bonding at Pt nuclei.[7] The coupling constant ratio, **7a**/**6a** = 1·4, is close to the ratio 1·5 of **7a**/**6a** in *6s-character* for Pt^{II} (*dsp*^{2}) and Pt^{IV} (*d*^{2}*sp*^{3}). A similar trend has been observed by Pregosin and Venanzi in the case of ^{195}Pt—^{31}P couplings.[22] Correlations of this type can be applicable only when factors other than the hybridization at platinum are fixed. Thus, *trans*-ligand to BCP in **6a** is probably Cl^- which is *trans*-ligand to BCP in **7a**.

Electronic structure of the platinum-cyclopropenylidene bond

We have found that comparing coordinatively unsaturated species PdCl$_2$(BCP) and PdCl$_2$(ACP), the former is stronger than the latter in Lewis-acidity.[5c] This fact indicates that the metal is more electron deficient in the former species than in the latter one. The cationic complexes $[PtCl(PBu_3)_2(BCP)]^+ClO_4^-$ (**11a**) revealed a larger negative (< −2·0 V) reduction potential than tri-*t*-butylcyclopropenium perchlorate *t*-Bu(BCP)$^+ClO_4^-$ (−1·51 V) indicating that PtCl(PBu$_3$)$_2$ group stabilizes the positive charge on the C_3 core more effectively than *t*-Butyl group. It is usual in rationalizing this kind of experimental data to postulate a significant amount of π back-bonding. For example, the difference in Lewis-acidity between PdCl$_2$(BCP) and PdCl$_2$(ACP) might be attributable to the difference in π acidity between BCP and ACP. In this study, however, NMR parameters have afforded no indications for π back-bonding interaction in both BCP—Pt and ACP—Pt.

Next we would examine σ electronegativity of ligand carbons, i.e. an electron flow through σ linkage. There are indications that the C_3 core of the diaminocyclopropenium system is relatively electron rich due to the strong π donating property of the NR_2 group. In one study of cyclic voltammetry, [23b] $(R_2N)_3C_3^+$ did not reveal a reduction wave within low voltage limit of −3·0 V (vs. SCE), whereas two oxidation waves were observed at +11·12 V and +2·1 V indicating a generation of a trication. Acid catalyzed H/D exchange reaction of 2,3-bis(dialkylamino)cyclopropenium ion at C_1 also demonstrates the relatively electron rich property of C_1.[23c] Although the electron release from NR_2 occurs in the π system of ACP, it might reduce the net electronegativity of the carbene carbon. In the case of the BCP system, on the other hand, the C_3 core may be electron deficient being devoid of efficient electron releasing groups. Thus, the carbene carbon of BCP would be more electronegative than the carbene carbon of ACP.

In connection with the σ inductive series of ligand carbons, $^1J_{PtP}$ for $PtCl(PBu_3)_2R$ should be informative. As shown in Table 1, the *cis*-influence order of $PhC{\equiv}C^- > t\text{-}BuC{\equiv}C^- > C_6H_5^- > CH_3^-$ was obtained. The order can be directly correlated with the electronegativity[24] series of the ligand carbon. Although theory on the nmr *cis*-influence is not so clear as nmr *trans*-influence, the *cis*-influence order can be explained based on the idea presented by Allen, Pidcock and Waterhouse[25] saying that CH_3^- reveals lower nmr *cis*-influence than Cl^- in comparing $^1J_{PtP}$ of 1719 Hz and 1856 Hz for *cis*-$PtCl(CH_3)(PEt_3)_2$ and *cis*-$Pt(CH_3)_2(PEt_3)_2$, respectively. They explain the fact in terms of the higher value of $|\psi_{Pt(6s)}(0)|^2$ for the former complex than the latter, owing to the strong σ donor ability of CH_3^-. This approach seems quite successful in explaining the nmr *cis*-influence order observed in the present study, which can be correlated with the electronegativity order of the ligand carbon. The magnitude of the *cis*-influence of BCP is higher than ACP and the highest among the carbon ligands listed in Table 1. This fact indicates that BCP is stronger than ACP in σ electron-withdrawing property, and is strongest among the carbon ligand listed in Table 1.

Although π interaction comes to mind first in considering cyclopropenylidene metal complexes, it seems that the Pt—BCP and Pt—ACP bonds are almost pure σ linkage, and electron flow in Pt—C_1 occurs via the σ component rather than the π component. This might be partly due to the particularity of cyclopropenium derivatives, the σ polarizability of substitutents being much more effective than π delocalization of the positive charge over substituents in stabilizing the system.[26]

CONCLUSION

^{13}C- and ^{195}Pt-NMR parameters derived from both the series, $Pt(CP)_2L_m$ and *trans*-$PtCl(PBu_3)_2R$, afforded the information for the nature of platinum—CP bond as follows: (1) cyclopropenylidene derivatives reveal a strong nmr *trans*-influence indicating an appreciable σ donor power of the ligands. (2) pπ—dπ bonding interaction plays a minor role in Pt—cyclopropenylidene bonding, and hence, (3) the transmission of the electronic effects of the groups of cyclopropenylidene occurs mainly through σ linkage of the Pt—CP bonding.

Other results from the present study are as following. An excellent line through the origin was obtained between $^1J_{PtC}$ and the formal '*s*' % character of the carbon (C_1) directly bonded to Pt for a series *trans*-$PtCl(PBu_3)_2R$ in which the Pt—C bond is viewed as a pure σ-linkage. In the case where the ligand carbon possesses low lying π* orbital(s) which possibly form pπ—dπ bonding, the $^1J_{PtC}$ deviates from the relationship largely in a positive direction.

EXPERIMENTAL SECTION

All melting points were determined on a Yanagimoto micro melting point apparatus. Infrared spectra were measured with a JASCO A-102 or a HITACHI EPI-G3 spectrophotometer. ^{1}H-, ^{13}C-, ^{31}P- and ^{195}Pt-NMR were recorded on a JEOL JNM-FX90Q system and a Jeol JNM-GX 400. Chemical shifts in ^{1}H- and ^{13}C-NMR spectra were expressed in ppm unit relative to tetramethylsilane. Chemical shifts in ^{195}Pt-NMR spectra are reported in ppm relative to H_2PtCl_6 (D_20) and the negative signs denote higher field direction. Cyclic voltammograms were obtained on a Yanaco voltammetric analyzer Model P-1000. The elemental anlyses were performed at the Microanalysis Center of Kyoto University. Benzene and ether were distilled over sodium/benzophenone. Methylene chloride was distilled over calcium hybride. Tributylphospine was freshly distilled before use. Other chemicals were commercially available reagent grade and were used without futher purification.

cis-$PtCl_4(BCP)_2$ (*6a*)

A mixture of 1·3 g (7.7 × 10^{-3} mol) of di-*t*-butylcyclopropenone[26a] in 10 ml of oxalyl chloride was refluxed under argon for 1 hr, and then excess oxalyl chloride was removed by pumping. The residual di-*t*-butyldichlorocyclopropene was added to a suspension of 1·5 g (7·7 × 10^{-3} g atom) of platinum black in 25 ml of dry benzene. All the procedures were performed using a glove box to avoid the exposure of materials to air. The mixture was refluxed for 72 hr under positive Ar pressure (balloon). Unreacted platinum black was removed by filtration and washed with CH_2Cl_2. The filtrate and the CH_2Cl_2 layer were combined and concentrated *in vacuo* to give a pale yellow solid of crude **6a**. Recrystallization from CH_2Cl_2 afforded yellow crystals of **6a** (0·97 g, 1·5 × 10^{-3} mol, 19%): mp 218 °C (dec.); ^{1}H-NMR ($CDCl_3$) δ 1·51 (s, 36H); ^{13}C-NMR (CD_2Cl_2) δ 28·11, 35·26, 166·6 ($^{1}J_{\mathrm{PtC}}$ = 1040 Hz), 195·3; ^{195}Pt-NMR ($CDCl_3$) δ −715 ppm; IR (KBr) 2950, 1480, 1328, 1226, 1220 cm^{-1}. Analysis Calculated for $C_{22}H_{36}Cl_4Pt$: C, 41·45; H, 5·69; Cl, 22·25. Found: C, 41·50; H, 5·69; Cl, 22·19.

cis-$PtCl_2(BCP)_2$ (**7a**)

A mixture of 188 mg (2·95 × 10^{-4} mol) of **6a** and 56 mg (2·95 × 10^{-4} mol) of anhydrous $SnCl_2$ was stirred under argon at room temperature. After stirring for 1 hr, the yellow solution turned colorless. The remaining $SnCl_2$ was filtered off and the filtrate was evaporated under reduced pressure. The residual solid was washed with benzene and recrystallized from ether/MeOH to afford white crystals of **7a** (55 mg, 9·7 × 10^{-5} mol, 33%): mp 263 °C (dec.); ^{1}H-NMR ($CDCl_3$) δ 1·38; ^{13}C-NMR (CD_2Cl)δ 27·9, 34·7, 178·8 ($^{1}J_{\mathrm{PtC}}$ = 1438 Hz), 193·0; ^{195}Pt-NMR ($CDCl_3$) δ −3315 ppm; IR (KBr) 2950, 1474, 1370, 1330, 1230, 1176 cm^{-1}. Analysis Calculated for $C_{22}H_{36}Cl_2Pt$: C, 46·65; H, 6·41; Cl, 12·52. Found: C, 46·50; H, 6.35; Cl, 12·40.

trans-$PtCl_2(ACP)_2$ (**8b**)

Bis(diisopropylamino)cyclopropenium perchlorate (2·5 g, 7·5 × 10^{-3} mol) was suspended in 150 ml of anhydrous ether and warmed to 30 °C under argon. To the suspension was added 6 ml of *n*-butyllithium in hexane (1·6 M) with stirring, and after a few minutes the suspension turned homogeneous. The solution of bis(diisopropylamino)lithiocyclopenium perchlorate (**9**)[3d] thus obtained was transferred under argon to a constant pressure addition funnel and added dropwise over 0·5 hr to a stirred suspension of 1 g ($3{\cdot}8 \times 10^{-3}$ mol) of $PtCl_2$ in 60 ml of ether. After stirring for 10 hr, undissolved materials were filtered off and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure. Chromatography on silica gel with CH_2Cl_2 followed by recrystallization from ether/acetone afforded white crystals of **8b** (112 mg, $1{\cdot}52 \times 10^{-4}$ mol, 4%): mp > 300 °C (dec.); ^{1}H-NMR ($CDCl_3$) δ 1·55 (d, 48H), 3·74 (sept, 8H); ^{13}C-NMR (CD_2Cl_2) δ 21·5, 51·2 (br), 136·0 ($^1J_{PtC}$ = 986 Hz), 146·7; ^{195}Pt-NMR (CD_2Cl_2) δ −3150 ppm; IR (KBr) 2975, 2935, 2880, 1854, 1490, 1467, 1378, 1337, 1183, 1166, 1023, 648, 542, 502 cm^{-1}; FIR 324 cm^{-1}. Analysis Calculated for $C_{30}H_{56}Cl_2N_4Pt$: C, 48·77; H, 7·64; N, 7·58; Cl, 9·60. Found: C, 48·92; H, 7·74; N, 7·41; Cl, 9·58.

cis-$PtI_2(ACP)_2$ (7c) and *trans*-$PtI_2(ACP)_2$ (8c)

To a suspension of 500 mg ($9{\cdot}0 \times 10^{-4}$ mol) of PtI_2 (COD) in 10 ml of anhydrous ether was added a solution of bis(diisopropylamino)lithiocyclopropenium perchlorate (**9**)[3d] ($2{\cdot}97 = 10^{-3}$ mol) in 90 ml of ether at −5–0 °C under argon atmosphere. After 10 hr stirring at the same temperature, the solvent was removed under reduced pressure. The residue was idssolved in CH_2Cl_2 and treated with a saturated aqueous solution of NH_4Cl. The organic layer was evaporated and the residue was dissolved in 14 ml of CH_2Cl_2 and 10 ml of MeOH. To the solution was added 0·05 ml of CH_3COCl at room temperature. Ater 1 hr stirring, the solution was concentrated slowly under reduced pressure. During the concentration, a yellow solid precipitated. Successive recrystallization from MeOH afforded pale yellow crystals, a mixture of **7c** and **8c**, with a combined yield of around 20%. The **7c**/**8c** ratio of this stage determined by ^{195}Pt-NMR largely depended on the temperature during the procedure and/or other unknown factors. The isomers were separated by developing on a PLC (silica gel) with CH_2Cl_2/ether (50/1) at −15 °C. Both the isomers were recrystallized from acetone to afford their pale yellow crystals. The complex **7c** gradually isomerized to **8c** in solution, and therefore perfect purification of **7c** could not be attained. Spectroscopic and elemental analyses were performed on a sample of **7c** containing a few percent of **8c**.

7c. Yellow crystals; mp > 300 °C (dec.); ^{1}H-NMR ($CDCl_3$) δ 1·50 (d, 48H), 3·75 (m, 8H); ^{195}Pt-NMR ($CDCl_3$) δ −3922 ppm; IR (KBr) 2950, 1840, 1328, 1160 cm^{-1}; FIR 134 cm^{-1}; Analysis Calculated for $C_{30}H_{56}I_2N_4Pt$: C, 39·09; H, 6·12; N, 6·08; I, 27·54. Found: C, 39·38; H, 6·26; N, 6·08; I, 27·74.

8c. Yellow crystals; mp > 300 °C (dec.); ^{1}H-NMR ($CDCl_3$) δ 1·49 (d, 48H), 3·79 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 22·8, 51·0, 131·8 ($^1J_{PtC}$ = 935 Hz), 146·6; ^{195}Pt-NMR ($CDCl_3$) δ −4718 ppm; IR (KBr) 2950, 1840, 1328, 1160 cm^{-1}; FIR 193 cm^{-1}. Analysis Calculated for $C_{30}H_{56}I_2N_4Pt$: C, 39·09; H, 6·12; N, 6·08; I, 27·54. Found: C, 39·13; H, 6·17; N, 6·07; I, 27·49.

trans-$PtICl(ACP)_2$ (8d)

To a stirred solution of 255 mg ($2{\cdot}77 \times 10^{-4}$ mol) of **8c** in 10 ml of CH_2Cl_2 was added a solution of 260 mg ($1{\cdot}01 \times 10^{-3}$ mol) of CF_3SO_3Ag in 10 ml of CH_3CN at room temperature. After stirring for 3 hr, precipitated silver iodide was filtered off, and to the filtrate was added 1·34 g ($8{\cdot}08 \times 10^{-3}$ mol) of Et_4NCl. The slightly yellow solution was stirred at room temperature for 1 hr, and concentrated to dryness *in vacuo*. To the residue was added 20 ml of CH_2Cl_2, and the solution was stirred for 10 hr. The mixture was washed with water, and the organic layer was dried over anydrous Na_2SO_4. After removal of the solvent, chromatography of the residue on silica gel with CH_2Cl_2 followed by recrystallization from ether/Ch_2Cl_2 afforded yellow crystals of **8d** (32 mg, $3{\cdot}85 \times 10^{-5}$ mol, 14%): mp > 300 °C (dec.); ^{1}H-NMR

($CDCl_3$) δ 1·55 (s, 48H), 3·77 (m, 8H); ^{195}Pt-NMR (CD_2Cl_2) δ −3928 ppm; IR (KBr) 2975, 2930, 2875, 1850, 1487, 1455, 1336, 1183, 1162, 1020, 890, 646, 542, 500 cm^{-1}. Analysis Calculated for $C_{30}H_{56}ClIN_4Pt$: C, 43·40; H, 6·80. Found: C, 43·67; H , 6·74.

cis-$PtCl_2(PBu_3)$(BCP) (10)

A mixture of 215 mg (1·29 × 10^{-3} mol) of di-*t*-butylcyclopropenone and 5 ml of oxalyl chloride was refluxed under argon for 1 hr, and then excess oxalyl chloride was removed by pumping. To the residue was added a solution of 600 mg (6.41 × 10^{-4} mol) of $Pt_2Cl_4(PBu_3)_2$[27] in 10 ml of dry benzene; and the mixture was refluxed under argon for 17 hr. Chromatography of the reaction mixture on silica gel with CH_2Cl_2/ether (1/1) followed by recrystallization from pentane/ethyl acetate afforded 163 mg (2·64 × 10^{-4} mol) of white crystals (22%): mp 147 °C; ^{1}H-NMR ($CDCl_3$) δ 0·90 (m, 9H), 1·46 (s, 18H), 1·46 (m, 18H); ^{13}C-NMR (CD_2Cl_2) δ 13·25 (s), 23·43 (t, J = 19 Hz), 24·09 (s), 25·85 (with satellites J = 29 Hz), 27·22 (s), 34·21 (s), 184·83 (d, $^2J_{PPtC}$ = 7·4 HZ, $^1J_{PtC}$ = 1400 Hz), 192·56 ($^2J_{PtCC}$ = 10 Hz); ^{31}P-NMR ($CDCl_3$) δ +1·74 ppm ($^1J_{PtP}$ = 3604 Hz); IR(KBr) 2960, 2925, 2875, 1485, 1466, 1350, 1180, 1100, 910, 733, 620, 465 cm^{-1}. Analyses Calculated for $C_{23}H_{45}Cl_2PPt$: C, 44·66; H, 7·33; Cl, 11·46; P, 5·01, Found: C, 44·38; H, 7·31; Cl, 11·67; P, 4·73.

trans-$[PtCl(PBu_3)_2(BCP)]^+ClO_4^-$ (11a)

To a solution of 139 mg (2·25 × 10^{-4} mol) of **10** in 2 ml of benzene was added 0·06 ml of PBu_3. After stirring for 5 minutes the solvent was removed, and the residue was dissolved in 3 ml of CH_2Cl_2 and shaken with 5 ml of aqueous saturated $KClO_4$. The CH_2Cl_2 layer was washed with three 2 ml portions of water and dried over anhydrous Na_2SO_4. Removal of solvent and crystallization from ether/CH_2Cl_2 afforded 164 mg (1·85 × 10^{-4} mol) of white crystals (66%): mp 167 °C (dec.); ^{1} H-NMR (CD_2Cl_2) δ 0·89 (m, 18H), 1·47 (s, 18H), 1·47 (m, 36H); ^{13}C-NMR (CD_2Cl_2) δ 13·25 (s), 21·48 (center of 5 resonances), 23·89 (t, J = 7·4 Hz), 26·11 (with satellites J = 22 Hz), 27·29 (s), 34·60 (s), 184·73 ($^1J_{PtC}$ = 1369 Hz, $^2J_{PPtC}$ = 8·8 Hz), 194·98 ($^3J_{PPtCC}$ = 1·5 Hz); ^{195}Pt-NMR ($CDCl_3$) δ −4236 ppm ($^2J_{PtP}$ = 2250 Hz); ^{31}P-NMR ($CDCl_3$) δ +7·66 ppm; IR (KBr) 2960, 2925, 2875, 1480, 1467, 1343, 1330, 1095, 907, 620, 445 cm^{-1}. Analyses Calculated for $C_{35}H_{72}Cl_2P_2Pt$: C, 47·51; H, 8·20; Cl, 8·01; P, 7·00. Found: C, 47·56; H, 8·46; Cl, 8·06; P, 6·72.

Preparation of *trans*-$PtCl(PBu_3)_2L$; 12a (L = t-BuC≡C), 14b (L = C_6H_5), 15b (L = Ch_3)

12a was prepared by modification of the procedure to synthesize *trans*-PtCl(C≡CPh) (PR_3) reported by Chatt and Shaw[9a,b]. **14b**[9a] and **15b**[9c] were prepared according to the method indicated in literature using PBu_3 in place of various phosphines in their descriptions.

trans-$PtCl(PBu_3)_2$(C≡CBu-t) (12a)

Sodium amide in liquid ammonia was prepared by the usual manner from 0·1 g of sodium (4·35 × 10^{-3} mol) in liquid ammonia (*ca*. 30 ml). To this was added 0·3 g (3·60 × 10^{-3} mol) of *t*-butylacetylene. After stirring for 3 hr at −30 °C, 2·14 g (3·19 × 10^{-3} mol) of *trans*-$PtCl_2$ $(PBu_3)_2$[28] was added. After stirring for 12 hr, anhydrous NH_4Cl (0·4 g) was added and the liquid ammonia allowed to evaporate. The residue was extracted with CH_2Cl_2 and washed with water. The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4, the solvent was evaporated, and the residue was chromatographed on silica gel with $CHCl_3$ to yield 0·3 g of colorless viscous liquid (13%): ^{1}H-NMR ($CDCl_3$) δ 0·91 (m, 18H), 1·15 (s, 9H), 1·47 (m, 24H), 1·93 (m, 12H); ^{13}C-NMR ($CDCl_3$) δ 13·46, 21·54 (center of 5 resonances), 23·98 (t, J = 6·7 Hz), 25·76 (with satellites J = 21 Hz), 29·23, 31·99 with satellites J = 11 Hz), 63·08 (t, $^{2}J_{PPtC}$ = 15 Hz), 107·68; ^{195}Pt-NMR (CD_2Cl_2) δ −4453 ppm ($^{1}J_{PtP}$ = 2419 Hz, $^{1}J_{CPt}$ = 1413 Hz); ^{31}P-NMR ($CDCl_3$) δ + 6·67 ppm; IR (neat) 2960, 2925, 2865, 2120 (C≡C), 1468, 1252, 1092, 902, 720, 528, 440 cm^{-1}. Analyses Calculated for $C_{30}H_{63}ClP_2Pt$: C, 50·30; H, 8·86; P, 8·65. Found: C, 50·04; H, 9·97; P, 8·74.

***trans*-$PtCl(PBu_3)_2(C_6H_5)$ (14b)**

White crystals; mp 70–71 °C; ^{1}H-NMR ($CDDl_3$) δ 0·93 (m, 18H), 1·49 (m, 36H), 6·9–7·4 (m, 5H); ^{13}C-NMR (CD_2Cl_2) δ 13·8 (s), 21·4 (center of 5 resonances), 24·5 (t, J = 6·7 Hz), 26·1 (with satellites J = 22 Hz), 121·7 ($^{4}J_{PtCCCC}$ = 15 Hz), 127·7 ($^{3}J_{PtCCC}$ = 73 Hz), 137·6 ($^{2}J_{PtCC}$ = 4·9 Hz), 138·3 ($^{1}J_{CPt}$ = 935 Hz, $^{2}J_{CPtP}$ = 9·2 Hz); ^{195}Pt-NMR ($CDCl_3$) δ −4267 ppm ($^{1}J_{PtP}$ = 2771 Hz); ^{31}P-NMR ($CDCl_3$) δ +6·20 ppm; IR (KBr) 3050, 2970, 2925, 2865, 1574, 1462, 1207, 1090 cm^{-1}. Analysis Calculated for $C_{30}H_{59}ClP_2Pt$: C, 50·59; H, 8·35; Cl, 4·98. Found: C, 50·82; H, 8·27; Cl, 5·01.

***trans*-$PtCl(PBu_3)(CH_3)$ (15b)**

Colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 0·29 (t, 3H, $^{2}J_{PtCH}$ = 84 Hz, $^{3}J_{PPtCH}$ = 6·4 Hz), 0·90 (m, 18H), 1·42 (m, 24H), 1·80 (m, 12H); ^{13}C-NMR ($CDCl_3$) 6 −23·7 (t, $^{2}J_{PPtC}$ = 6·8 Hz, $^{1}J_{PtC}$ = 694 Hz), 13·31 (s), 20·51 (center of 5 resonances), 23·76 (t, J = 5·9 Hz), 25·67 (with satellites J = 22 Hz); ^{195}Pt-NMR ($CDCl_3$) δ −4482 ppm ($^{1}J_{PtP}$ = 2795 Hz); ^{31}P-NMR ($CDCl_3$) δ +7·80 ppm; IR (neat) 2960, 2930, 2865, 1468, 1210, 1093, 900, 723, 550, 440 cm^{-1}. Analysis Calculated for $C_{25}H_{57}ClP_2Pt$: C, 46·18; H, 8·84; P, 9·53; Cl, 5·45; Found: C, 45·95; H, 8·71; P, 9·60; Cl, 5·35.

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