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cis-π-ACETYLENIC METHYLPLATINUM(II) COMPLEXES

HOWARD C. CLARK* and K. von WERNER

Department of Chemistry, University of Western Ontario, London, Ontario (Canada)

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Summary

Diorganobis(1-pyrazolyl) borate methylplatinum(II) complexes of the type $(R_2Bpz_2)PtMeL$ (R = C_2H_5 or C_6H_5, pz = 1-pyrazolyl and L = tertiary phosphine, isocyanide or acetylene) have been prepared. Stable acetylene complexes containing $C_6H_5C{\equiv}CC_6H_5$ and $C_6H_5C{\equiv}CCH_3$ are obtained which are inert towards insertion of the acetylene into the Pt—CH_3 bond. On the other hand, dimethylacetylene dicarboxylate and hexafluorobut-2-yne do not give analogous complexes but give directly the platinum(methylvinylic) insertion products. Spectroscopic data and bonding are discussed for neutral four- and five-coordinate methylplatinum(II) acetylene complexes.

Introduction

Recent studies [1,2], including kinetic investigations [3,4] have demonstrated unambiguously that, in many cases, the insertion of olefins or acetylenes into Pt—H or Pt—C bonds occurs first by the substitution of the ligand *trans* to hydride or alkyl, followed by rearrangement of the resulting four-coordinate species to give, ultimately, the inserted product. Formally at least, this would appear to involve a *trans*→*cis* isomerization in order to generate a *cis*-intermediate which then undergoes the migratory rearrangement of insertion. The above studies were concerned primarily with cationic platinum(II) species in which activation of the olefin or acetylene by coordination to the electron-poor platinum atom would occur. For neutral complexes, less definitive information is available. Five-coordinate methylplatinum(II) acetylene complexes are sufficiently stable to be isolated [5], but on long-standing insertion occurs; the insertion mechanism is not clear. In contrast, analogous five-coordinate hydrotris(pyrazolyl) borate methylplatinum(II) acetylene complexes, which also have the Pt—CH_3 bond *cis* to the coordinated acetylene, are extremely stable and do not undergo insertion at temperatures up to the decomposition point [6]. Comparison of the behaviour with regard to insertion of cationic four-coordinate

TABLE 1

ANALYTICAL DATA

R	Complex	Analysis found (calcd.) (%)			M.p. (°C)	Colour	Yield (%)
		C	H	N			
C_2H_5	$[Pt[R_2Bpz_2](CH_3)]_2(COD)$	38.46 (38.56)	5.47 (5.39)	12.31 (11.99)	182-184 [a]	white	92
C_2H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{\equiv}CC_6H_5)$	50.88 (50.77)	4.99 (4.94)	9.30 (9.47)	126	pale orange	95
C_2H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{\equiv}CCH_3)$	45.69 (45.38)	5.28 (5.14)	10.68 (10.58)	150-151	pale yellow	93
C_2H_5	$Pt[R_2Bpz_2](CH_3)(p\text{-}CH_3C_6H_4NC)$	43.05 (43.03)	5.07 (4.94)	13.40 (13.21)	102-103	white	92
C_2H_5	$[Pt[R_2Bpz_2](CH_3)]_2[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]$	47.19 (47.07)	5.13 (5.10)	9.20 (9.15)	229	white	89
C_2H_5	$Pt[R_2Bpz_2](CH_3)[P(CH_3)_2C_6H_5]$	41.59 (41.39)	5.42 (5.48)	10.08 (10.16)	92	white	72
C_2H_5	$Pt[R_2Bpz_2](CH_3)[P(C_6H_5)_3]$	51.75 (51.57)	5.08 (5.07)	8.47 (8.29)	158	white	83
C_2H_5	$Pt[R_2Bpz_2](CH_3)(CO)$	33.09 (32.67)	3.89 (4.34)	12.68 (12.70)	50	white	72
C_2H_5	$Pt[R_2Bpz_2][C(CO_2CH_3){=}C(CO_2CH_3)CH_3]$	36.57 (36.77)	4.42 (4.54)	9.85 (10.09)	190 [a]	white	40
C_2H_5	$Pt[R_2Bpz_2][C(CF_3){=}C(CF_3)CH_3][P(C_6H_5)_3]$	47.29 (46.99)	4.13 (4.78)	6.76 (6.64)	191	white	40
C_6H_5	$[Pt[R_2Bpz_2](CH_3)]_2(COD)$	48.70 (49.03)	4.24 (4.47)	9.91 (9.94)	>230 [a]	white	53
C_6H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{\equiv}CCH_3)$	53.57 (53.77)	4.37 (4.35)	8.97 (8.96)	181-182	pale yellow	86
C_6H_5	$Pt[R_2Bpz_2][C(CO_2CH_3){=}C(CO_2CH_3)CH_3]$	44.49 (46.10)	3.85 (3.87)	7.92 (8.60)	>270 [a]	white	49
	$Pt(CH_3)(C_6H_5)(COD)$	45.99 (45.56)	5.11 (5.10)		158 [a]	white	79

[a] Decomposition.

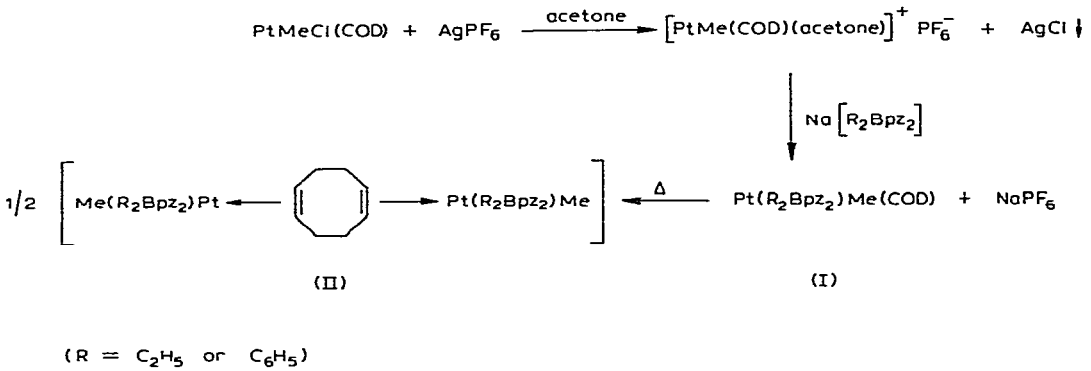
platinum(II) species with neutral five-coordinate species suggests that the geometry and coordination number about platinum are important in determining the ease of insertion. We now describe the preparation and properties of neutral, four-coordinate diorganobis(pyrazolyl) boratemethylplatinum(II) acetylene complexes in which the Pt—CH_3 and coordinated acetylene are *cis* to one another.

Results and discussion

Preparation

In order to prepare neutral, four-coordinate bis(1-pyrazolyl) borate complexes, a reactive precursor $Pt[R_2Bpz_2]MeL'$ was needed in which L' could readily be displaced by a variety of neutral donors, L. A suitable synthesis for such a precursor was devised, based on the known [7] reactivity of the cation $[PtMe(COD)(solvent)]^+$ (COD = 1,5-cyclooctadiene) (see Scheme 1).

SCHEME I



It is interesting to note that while this reaction sequence proceeded smoothly for R = C_2H_5 or C_6H_5, the use of sodium tetraphenyl borate instead of $Na(R_2Bpz_2)$ resulted in a rapid phenyl transfer with formation of PtMePh(COD). The intermediate I with R = C_2H_5, readily lost cyclooctadiene to give II as an insoluble white product. For R = C_6H_5, this conversion of I to II is slow at room temperature but becomes rapid above 40°C. The formulation of the compounds II as binuclear species is consistent with their analytical data and low solubility which also suggest that the COD molecule is functioning as a bridging ligand. Although a polymeric structure might appear possible, it would require the bis(pyrazolyl) borate group to act as an *exo* bidentate ligand; such behaviour has not yet been observed and it would in any event impose great strain on the N—B—N bond angle. An analogous compound, probably with the same basic structure has been prepared [8] by the same method using diethyl dithiocarbamate to give $\{[(C_2H_5)_2NCS_2]PtCH_3\}_2COD$.

Although the compounds II are essentially insoluble in dichloromethane, solution occurs readily when a donor ligand L is added to the suspension to give crystalline complexes III by displacement of COD (eqn. 1) (see Table 1 for analytical data, and Table 2 for spectroscopic data).

(Continued on p. 352)

TABLE 2

SPECTROSCOPIC DATA

Multiplicity: d = doublet, m = multiplet
IR relative intensities: w = weak, m = medium, s = strong, vs = very strong

R	Complex	^{1}H NMR					
		Methylplatinum		Pyrazole ring[a]			
				H(4)			
				Ring A		Ring B	
		δ(ppm)	^2J(Pt—H) (Hz)	δ(ppm)	^4J(Pt—H) (Hz)	δ(ppm)	^4J(Pt—H) (Hz)
C_2H_5	Pt[R_2Bpz$_2$](CH$_3$)($C_6H_5C{\equiv}CC_6H_5$)	0.77	76.0	5.96(2.2)		6.28(2.3)	14.7
C_2H_5	Pt[R_2Bpz$_2$](CH$_3$)($C_6H_5C{\equiv}CCH_3$)	0.66	75.0	6.04(2.2)	8.5	6.25(2.4)	14.6
C_2H_5	Pt[R_2Bpz$_2$](CH$_3$)(*p*-$CH_3C_6H_4NC$)	0.78	74.4	6.19(2.2)	8.6	6.21(2.3)	11.1
C_2H_5	[Pt[R_2Bpz$_2$](CH$_3$)]$_2$[$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$]	0.90	73.5	5.66(2.2)		6.20m	
C_2H_5	Pt[R_2Bpz$_2$](CH$_3$)[$P(CH_3)_2C_6H_5$]	0.56[f]	73.0	5.87(2.3)	~9	6.12m	
C_2H_5	Pt[R_2Bpz$_2$](CH$_3$)[$P(C_6H_5)_3$]	0.48[g]	72.0	5.64(2.3)	~10	6.15m	
C_2H_5	Pt[R_2Bpz$_2$](CH$_3$)(CO)	1.08	71.4	6.23(2.4)	~10	6.23(2.4)	
C_2H_5	Pt[R_2Bpz$_2$][$C(CO_2CH_3){=}C(CO_2CH_3)CH_3$]			6.03(2.4)		6.23(2.3)	
C_2H_5	Pt[R_2Bpz$_2$][$C(CF_3^1){=}C(CF_3^2)CH_3$][$P(C_6H_5)_3$]			5.66(2.4)		6.20m	
C_6H_5	Pt[R_2Bpz$_2$](CH$_3$)($C_6H_5C{\equiv}CCH_3$)	0.43	75.8	6.07(2.2)		6.30(2.3)	
C_6H_5	Pt[R_2Bpz$_2$][$C(CO_2CH_3){=}C(CO_2CH_3)(CH_3)$] Pt(CH$_3$)($C_6H_5$)(COD)	0.84	83.2				

TABLE 2 (continued)

R	Complex	^{1}H NMR				IR (cm^{-1})
		Pyrazole ring[a]	Ethyl boron		Other resonances (δ(ppm)) and couplings (J(Hz))	
		H(3.5) δ(ppm)	$\delta(CH_2)$ (ppm)	$\delta(CH_3)$ (ppm)		
C_2H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{\equiv}CC_6H_5)$	7.08(2.0), 7.57(2.2), 7.77(2.3), 7.85(2.2)	1.20	0.79		ν(C≡C)1965w-m
C_2H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{\equiv}CCH_3)$	7.09(2.0, 7.59(2.2), 7.71[b]	1.1[c]	~0.9[c]	$\delta(CH_3)$2.43, ^3J(Pt—H)43.2	ν(C≡C) 2023w-m
C_2H_5	$Pt[R_2Bpz_2](CH_3)(p\text{-}CH_3C_6H_4NC)$	[d]	1.16	0.79	$\delta(CH_3)$2.38	ν(N≡C) 2196vs
C_2H_5	$[Pt[R_2Bpz_2](CH_3)]_2[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]$	6.51(2.0)[d]	[e]	[e]	$\delta(CH_2)$2.77m	
C_2H_5	$Pt[R_2Bpz_2](CH_3)[P(CH_3)_2C_6H_5]$	6.83(2.0)[d]	1.3	0.77	$^2(CH_3)$1.68d, ^2J(P—H)10, ^3J(Pt—H)42	
C_2H_5	$Pt[R_2Bpz_2](CH_3)[P(C_6H_5)_3]$	6.23(2.1)[d]	1.40	0.89		
C_2H_5	$Pt[R_2Bpz_2](CH_3)(CO)$	7.49(2.0), 7.60(2.2), 7.64[b]	1.1	0.77		ν(C≡O) 2090vs
C_2H_5	$Pt[R_2Bpz_2][C(CO_2CH_3)=C(CO_2CH_3)CH_3]$	7.29(2.2), 7.46[b], 7.57(2.4)	[e]	[e]	$\delta(CH_3)$2.66, ^4J(Pt—H)15.0, $\delta(OCH_3)$ 3.13, 3.68	ν(C=O) 1706s, 1552vs, ν(C=C)1609m, ν(C—OC) 1298s,
C_2H_5	$Pt[R_2Bpz_2][C(CF_3^1)=C(CF_3^2)CH_3][P(C_6H_5)_3]$	6.78(2.2)[d]	1.28	0.84	$\delta(CH_3)$1.98m, ^4J(Pt—H)~14, $\delta(CF_3^1)$ 49.6, $\delta(CF_3^2)$61.5[h], $^5J(F^1F^2)$15.0	ν(C=C) 1605w, broad, ν(C—F)1283m, 1234s, 1142s, 1121vs
C_6H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{=}CCH_3)$	7.40, 7.49[b], 7.92			$\delta(CH_3)$1.78, ^3J(Pt—H)41.6	ν(C≡C) 2014w-m
C_6H_5	$Pt[R_2Bpz_2](CH_3)(C_6H_5C{\equiv}CCH_3)$					
C_6H_5	$Pt[R_2Bpz_2][C(CO_2CH_3){=}C(CO_2CH_3)(CH_3)]$				$\delta(CH_3)$2.24, ^4J(Pt—H)~14.5, $\delta(OCH_3)$ 3.34, 3.70	ν(C=O) 1700s, 1558vs, ν(C=C)1618s, ν(C—OC) 1298s, 1270vs
	$Pt(CH_3)(C_6H_5)(COD)$				$\delta(CH_2)$2.44, 2.54 δ(CH)4.98, 5.22	ν(C=C) (aromatic) 1569m

[a] J(H—H)(Hz) given in parentheses. [b] 2 protons. [c] Very broad, unresolved. [d] Downfield region obscured by phenyl resonances. [e] Very complex signals. [f] ^3J(P—H) 4.2 [g] ^3J(P—H) 4.2. [h] Upfield from internal $CFCl_3$.

$$II + 2\,L \rightarrow \underset{(III)}{2\,Pt(R_2Bpz_2)MeL} + COD \qquad (1)$$

(for R = C_2H_5 ; L = $C_6H_5C{\equiv}CC_6H_5$, $C_6H_5C{\equiv}CCH_3$, *p*-$CH_3C_6H_4NC$, $P(CH_3)_2C_6H_5$, $P(C_6H_5)_3$, CO and for R = C_6H_5 ; L = $C_6H_5C{\equiv}CCH_3$)

Such reactions where L is 2-butyne, styrene, maleic anhydride, or dimethyl fumarate were very slow and appeared to be reversible; attempts at product isolation resulted only in recovery of II. However, II reacted readily with phenylacetylene, propiolic acid methyl ester, or tetracyanoethylene to give dark solutions from which no identifiable compounds could be isolated.

In an attempt to prepare a five-coordinate complex analogous to $Pt(RBpz_3)MeL$, III (R = C_2H_5 ; L = $C_6H_5C{\equiv}CC_6H_5$) was treated with excess pyrazole but only the starting materials were recovered. In a further attempt to form a five-coordinate complex, III (R = C_2H_5) was treated with 1,2-bis(diphenylphosphino)ethane(diphos) in a ratio diphos/Pt = 1/1. A crystalline complex IV was obtained (eqn. 2), its formulation as a binuclear, diphos bridged species being based on its elemental analyses and NMR data.

$$II + Ph_2PCH_2CH_2PPh_2 \rightarrow \underset{(IV)}{[R_2Bpz_2]Pt(Ph_2PCH_2CH_2PPh_2)Pt[R_2Bpz_2]} + COD \qquad (2)$$

Again, the low solubility of IV in dichloromethane, contrasts the high solubility of III but resembles that of II and is consistent with the binuclear formulation.

Acetylene insertions into the platinum—methyl bond

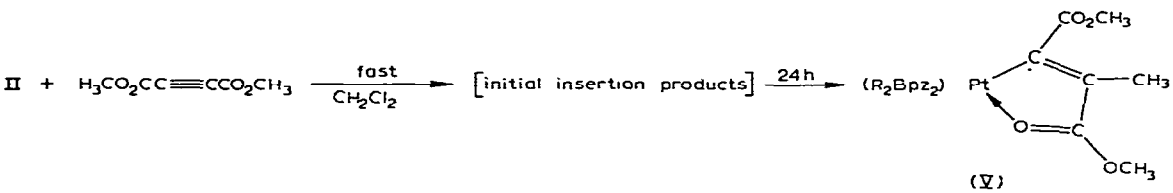
The compounds III (L = $C_6H_5C{\equiv}CC_6H_5$ or $C_6H_5C{\equiv}CCH_3$) were surprisingly inert towards insertion of the acetylene into the Pt—C bond. Thus the diphenylacetylene complex was recovered unchanged after being refluxed in benzene solution for 2 days. In contrast, when hexafluorobut-2-yne was allowed to react with a dichloromethane suspension of II (R = C_2H_5) at room temperature, insertion occurred very rapidly, probably via initial formation of a four-coordinate π-complex similar to III. The proton resonance spectrum of such a reaction mixture in $CDCl_3$ solution showed a methyl signal at 2.53 ppm while no peak corresponding to a methylplatinum group could be observed. Because of difficulties in crystallizing this reaction product from solution, it was isolated as its triphenylphosphine derivative.

$$\tfrac{1}{2}\,II\ (R = C_2H_5) + CF_3C{\equiv}CCF_3 \rightarrow \left[(R_2Bpz_2)Pt(CH_3)(CCF_3)(C{=}CF_3)\right] \xrightarrow{fast} (R_2Bpz_2)PtC(CF_3){=}C(CF_3)CH_3$$

$$(R_2Bpz_2)PtC(CF_3){=}C(CF_3)CH_3 \xrightarrow{PPh_3} \underset{(IV)}{(R_2Bpz_2)Pt(PPh_3)(CH_3)(CF_3C{=}CF_3)}$$

The close similarity of the spectroscopic data of IV with those of other platinum(II) derivatives containing the same vinylic ligand [3] confirms that only *cis* addition of Pt—CH_3 across the acetylenic triple bond has occurred. This is consistent with a mechanism involving a planar, four-centred transition state composed of platinum, methyl carbon and the two acetylenic carbons.

Dimethylacetylene dicarboxylate, which likewise possesses electron-withdrawing acetylenic substituents, also gave very rapid insertion. The ^1H NMR spectrum (in $CDCl_3$) of the reaction mixture was at first rather complex, but gradually changed with the formation of two products. One of them ($\delta(=CCH_3)$ 2.15 ppm, $J(Pt—CH_3)$ ~3 Hz) could not be isolated but is probably a *cis* vinylic insertion product. The other far less soluble product was isolated pure and assigned structure V on the basis of its spectroscopic data. Interestingly, the rate of formation of V is markedly dependent on the solvent, the rate changing in the order $CH_2Cl_2 > CHCl_3 \gg (CH_3)_2CO$.



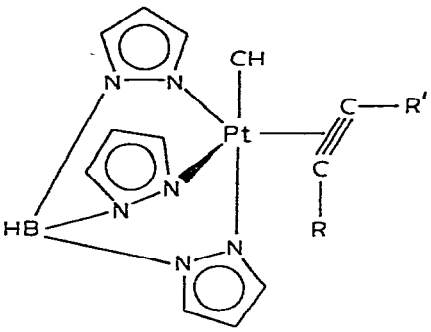
The large coupling constant (~15 Hz) between the $=CCH_3$ methyl protons and ^{195}Pt is indicative of a *trans* vinylic geometry. The infrared spectrum shows two intense $\nu(C=O)$ absorptions with a considerable separation (142 cm^{-1}); the position of the lower band at 1558 cm^{-1} strongly suggests the coordination of one carbonyl group to platinum. The resulting five-membered chelate ring should then make V rather inert towards substitution, and this is consistent with the fact that V could be recovered unchanged from solutions containing a large excess of triphenylphosphine. Other compounds containing related five-membered rings of the form Pt—CR_2—X—C(R)=O (X = O or NH) have recently been described [9]. In the present case, the mechanism of ring formation is unclear. While the observed formation of the *cis* vinylic derivative would be expected for a four-centred transition state, isomerization of this form to the *trans* vinylic species would seem to be highly demanding energetically. However, such isomerization has been described recently [10] for comparable rhodium species.

Reactions of the cationic species $[PtCH_3(L—L)solvent]^+$ (L—L = diars or diphos) with the acetylenes RC≡CR (R = CF_3 or CO_2CH_3) give products [11] similar to those just described.

Bonding

On the basis of spectroscopic data it is interesting to compare the metal—acetylene bonding in four- and five-coordinate polypyrazolyl borate platinum(II) derivatives. An X-ray structural determination of III (R = C_2H_5, L = C_6H_5-C≡CC_6H_5) has revealed that the acetylene lies perpendicular to the molecular plane and adopts a *cis* bent configuration [12]. An earlier crystallographic study of the complex $Pt(HBpz_3)CH_3(CF_3C≡CCF_3)$ has shown the acetylene to

be located in the trigonal plane [13]. In both cases, therefore, the acetylene is at right angles to the Pt—CH_3 bond although *cis* to methyl with respect to platinum. On the basis of ^{1}H NMR data, structure VI has also been deduced [6] for other complexes containing unsymmetrically substituted acetylenes.



(VI)

Values of $\Delta\nu$(C≡C), which is the difference in the IR active stretching frequency ν(C≡C) for free and coordinated acetylene, are given for compounds of both types in Table 3.

The five coordinate compounds absorb ca. 115 cm^{-1} below the complexes III. A similar difference was found between the complexes *trans*-Pt(acetylene)-amine)Cl_2 [14] and Pt(acetylene)(ethylenediamine)Cl_2 [15]. Although IR frequencies, in the absence of other data, do not allow any conclusions to be drawn concerning the relative strength of the σ and π bonding components, the deviation of the acetylene ligand from its ground state is certainly larger in VI than in III. Thus, for the same oxidation number and with the same type of ligands, the type of bonding appears to depend on the coordination number and on the geometry of the complex. As was recently pointed out by Hartley, the characteristic features of the acetylene—metal bond are most adequately explained by molecular orbital theory [16]. In particular, the same set of orbitals can be used to describe the bonding in VI and in complexes PtL_2(RC≡CR) (L = tertiary phosphine), though in VI less electron density will be transferred to the acetylene due to the higher oxidation state of the metal.

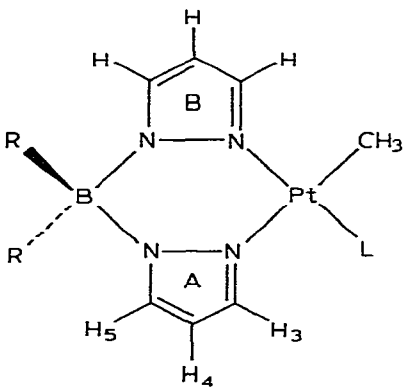
A further point of interest is the different ease of insertion encountered with bis- and tris(pyrazolyl) borate complexes. Since structural studies [12,13]

TABLE 3

$\Delta\nu$(C≡C) FOR POLYPYRAZOLYL BORATE PLATINUM ACETYLENE COMPLEXES

Complex	$\Delta\nu$(C≡C) (cm^{-1})
Pt[$(C_2H_5)_2Bpz_2$](CH_3)($C_6H_5C{\equiv}CC_6H_5$)	258
Pt[$HBpz_3$](CH_3)($C_6H_5C{\equiv}CC_6H_5$) [6]	405
Pt[$(C_2H_5)_2Bpz_2$](CH_3)($C_6H_5C{\equiv}CCH_3$)	206
Pt[$(C_6H_5)_2Bpz_2$](CH_3)($C_6H_5C{\equiv}CCH_3$)	215
Pt[$HBpz_3$](CH_3)($C_6H_5C{\equiv}CCH_3$) [6]	372

show that, for both classes of compounds the stable geometry contains the Pt—C and C≡C bonds in orthogonal arrangements, rotation of the acetylene into a more suitable geometry for insertion may be required for facile insertion. For the compounds III, the values of $\Delta\nu$(C≡C) may indicate a smaller π-component to the platinum—acetylene bond thus giving a lower energy barrier for rotation of the acetylene. It is also clear, considering the cases where L = $C_6H_5C{\equiv}CC_6H_5$ and L = $CF_3C{\equiv}CCF_3$, that electron-withdrawing substituents on the acetylene appear to have a much greater labilizing effect towards insertion for compounds III. It is also likely, for the tris(pyrazolyl) borate complexes, that insertion with rearrangement to a square planar inserted product is made difficult by the chelate nature of the ligand.



The ^{1}H NMR spectra of complexes III (see Table 2) show two distinct sets of pyrazolyl protons arising from the two different rings: this indicates a stable, non-fluxional structure for all compounds in solution at 30°C. The H(3) and H(5) proton resonances appear approximately as doublets, and the H(4) signals as triplets due to coupling with the neighbouring protons. The H(4) resonance showing the smaller coupling constant to platinum is most likely associated with ring A *trans* to the methyl group (i.e., *trans* to the ligand with the higher *trans* influence). For the compounds with a $C_6H_5C{\equiv}CC_6H_5$ or $C_6H_5C{\equiv}CCH_3$ ligand a simple double resonance experiment showed the proton A to absorb at higher field than the corresponding B protons. In the presence of phosphine ligands having at least one phenyl substituent, the ring A H(4) and to an even greater extent the H(3) resonances show a remarkable high field shift which could be due to anisotropic shielding caused by the phenyl rings.

The observed values for methyl to platinum coupling constants ^2J(Pt—H) lie in the range normally encountered in planar platinum(II) complexes. Although it is tempting to try to correlate our data with the known order of the *trans* influence in existing series of *trans* methylplatinum compounds, no obvious trends could be found.

With L = dimethylphenylphosphine, the two methyl groups attached to phosphorus are magnetically inequivalent for any non-planar arrangement of the six-membered ring formed by platinum, the pyrazolyl nitrogens and the boron atom. Surprisingly, the NMR spectrum of the complex at 30°C shows only one doublet resonance for the phosphine CH_3 protons. Two explanations, other than an accidental (and improbable) complete equivalence of the chem-

ical shifts, are possible: (*i*) the [Pt(N≡N)$_2$B]-ring may have a planar ground state, or (*ii*) an equilibrating process may occur which involves two equivalent conformational isomers (probably boat forms) and which is fast on the NMR time scale. The first of these explanations would seem unlikely.

The lack of unusual chemical shifts for the pyrazolyl ethyl protons combined with the absence of any pronounced lowering of ν(C—H) stretching frequencies suggests no or very little interaction between these ethyl substituents and the central metal. However, it should be noted that the structure determination [12] places a β-ethyl proton at a distance of 2.7 Å from platinum. While this is greater than that expected for a reasonably strong Pt—H interaction the possibility of a weaker interaction is not excluded.

Experimental

Sodium diethylbis(1-pyrazolyl) borate and sodium diphenylbis(1-pyrazolyl) borate were prepared by the method of Trofimenko [17,18]. Acetone was distilled from phosphorus pentoxide under nitrogen prior to use, other solvents were "Spectro-analyzed" grade.

Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona.

Nuclear magnetic resonance spectra were recorded on a Varian Associates HA-100 spectrometer at 100 MHz using chloroform-*d* solutions. Chemical shifts (δ) are reported in ppm, downfield from internal TMS, and coupling constants (J) are given in Hz.

Infrared spectra were recorded on a Perkin—Elmer 621 grating spectrometer, the samples being prepared as nujol mulls between KBr plates. The spectra were calibrated with polystyrene (accuracy ±3 cm^{-1}).

(a) Preparation of [Pt[(C$_2$H$_5$)$_2$Bpz$_2$](CH$_3$)]$_2$(COD)

To a stirred solution of PtCl(CH$_3$)(COD) (3.54 g, 10.0 mmol) in 60 ml of dried acetone was added $AgPF_6$ (2.52 g, 10.0 mmol) under nitrogen. After 15 min the silver chloride was allowed to coagulate and was filtered off to give a clear colorless solution. A solution of Na[(C$_2$H$_5$)$_2$Bpz$_2$] (2.26 g, 10.0 mmol) in 20 ml of acetone was added dropwise. The solvent was removed on a rotary evaporator and the white residue dried for 30 min at 40°C/0.1 Torr to get rid of most of the liberated COD. The solid was then stirred for 30 min in 50 ml of an ethanol/water mixture (3/1) to give crystals which were washed with water, acetone and diethyl ether.

(b) Preparation of [Pt[(C$_6$H$_5$)$_2$Bpz$_2$](CH$_3$)]$_2$(COD)

To a solution of 10.0 mmol [Pt(CH$_3$)(COD)(acetone)]PF_6, obtained as described in *a*, a solution of Na[(C$_6$H$_5$)$_2$Bpz$_2$] (3.22 g, 10.0 mmol) in 20 ml of acetone was added slowly. The solvent was evaporated under reduced pressure and the residue was extracted with three 20 ml portions of dichloromethane. From the combined extracts a light yellow oil was obtained by removing the CH_2Cl_2. It was dried for 1 h at 50°C/0.1 Torr, then heated under reflux in 50 ml of CH_2Cl_2/n-pentane (1/2) over-night. The crystalline product was isolated by filtration and washed with n-pentane and diethyl ether.

(c) Preparation of complexes $Pt[R_2Bpz_2](CH_3)L$ ($R = C_2H_5$, $L = C_6H_5C{\equiv}CC_6H_5$, $C_6H_5C{\equiv}CCH_3$, $p\text{-}CH_3C_6H_4NC$, $P(CH_3)_2C_6H_5$, $P(C_6H_5)_3$; and $R = C_6H_5$, $L = C_6H_5C{\equiv}CCH_3$)

To a suspension of $[Pt[(C_2H_5)_2Bpz_2](CH_3)]_2(COD)$ (235 mg, 0.25 mmol) in 10 ml of dichloromethane a stoichiometric amount (0.5 mmol) of the ligand of choice (90 mg $C_6H_5C{\equiv}CC_6H_5$, 58 mg $C_6H_5C{\equiv}CCH_3$, 59 mg $p\text{-}CH_3C_6H_4NC$, 69 mg $P(CH_3)_2C_6H_5$ or 131 mg $P(C_6H_5)_3$) was added with stirring. The starting material dissolved readily and 5 min later the solution was passed through a short (4 X 15 mm) florisil column. The solvent was removed by rotary evaporation to give an oil which smelled strongly of cyclooctadiene which was pumped off under high vacuum. The residue was dissolved in ca. 0.3 ml of dichloromethane, and n-pentane was added until the first crystals formed. The flask was cooled at —20° C for 24 h, the liquid was decanted and then the crystals were washed with 3 ml of ice-cold n-pentane. Recrystallization from CH_2Cl_2/n-pentane afforded the products as well-shaped needles or plates, which were very soluble in CH_2Cl_2, $CHCl_3$ and C_6H_6, soluble in $(C_2H_5)_2O$, but insoluble in n-pentane below 0° C.

Analogous diphenylbis(1-pyrazolyl) borate complexes can be obtained similarly, as shown by a reaction with methylphenylacetylene, starting with $[Pt[(C_6H_5)_2Bpz_2](CH_3)]_2(COD)$.

(d) Preparation of $Pt[(C_2H_5)_2Bpz_2](CH_3)(CO)$

Carbon monoxide was bubbled through a suspension in CH_2Cl_2 of II which dissolved within 2 min. Working up as in *c* resulted in the formation of a colourless oil, which was dried under vacuum and taken up in 0.5 ml n-heptane. The solution was kept for 1 week at —20° C to give large prisms.

(e) Preparation of $Pt[(C_2H_5)_2Bpz_2](CH_3)]_2[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]$

The complex was prepared as described in *c* from II and the phosphine. The product was recrystallized from dichloromethane/diethyl ether, and was soluble in CH_2Cl_2, sparingly soluble in $CHCl_3$, and insoluble in diethyl ether or n-pentane.

(f) Preparation of $Pt[R_2Bpz_2][C(CO_2CH_3){=}C(CO_2CH_3)(CH_3)]$ ($R = C_2H_5$, C_6H_5)

To a suspension of $[Pt[R_2Bpz_2](CH_3)]_2(COD)$ (0.25 mmol, R = C_2H_5 235 mg, R = C_6H_5 282 mg) in 10 ml of dichloromethane a solution of dimethylacetylenedicarboxylate (0.5 mmol, 71 mg) in 10 ml of CH_2Cl_2 was added dropwise. The yellow solution was heated under reflux for 1 h. After it had cooled to room temperature, it was passed through a florisil column, followed by elution with CH_2Cl_2. The solvent was reduced in volume to about 3 ml for R = C_2H_5 (10 ml for R = C_6H_5) and crystallization was initiated by addition of n-pentane. The flask was cooled at —10° C for 12 h. The product was isolated by decantation of solvents and was washed with diethyl ether.

(g) Preparation of $Pt[(C_2H_5)_2Bpz_2][C(CF_3){=}C(CF_3)CH_3]P(C_6H_5)_3$

$[Pt[(C_2H_5)_2Bpz_2](CH_3)]_2(COD)$ (0.25 mmol, 235 mg) in 10 ml of dichloromethane was vigorously stirred under hexafluorobutyne (~5 fold excess).

It dissolved within 10 min to give a pale yellow solution. After 1 h triphenylphosphine (0.5 mmol, 131 mg) was added, then 5 ml of n-pentane. The mixture was passed through a florisil column and was reduced in volume to about 3 ml and n-pentane was added until the solution became cloudy. The temperature was slowly lowered to −20° C and the crystals, which were obtained after two days, were recrystallized from dichloromethane/diethyl ether.

(h) Preparation of $Pt(CH_3)(C_6H_5)(COD)$

To a solution of 2.0 mmol $[Pt(CH_3)(COD)(acetone)]PF_6$ in 50 ml of acetone, prepared as under *a*, was added $Na[B(C_6H_5)_4]$ (2.0 mmol, 684 mg), dissolved in acetone. The mixture was stirred for 1 h. Evaporation of the solvent gave an oil which crystallized on stirring with 15 ml ethanol/water (2/1). The solid was filtered off, dried under vacuum and redissolved in dichloromethane. This solution was shaken with a small amount of active charcoal and filtered. Addition of n-pentane followed by cooling gave the complex as needles.

References

1 H.C. Clark and H. Kurosawa, Inorg. Chem., 11 (1972) 1275.
2 M.H. Chisholm and H.C. Clark, Accounts Chem. Res., 6 (1973) 202.
3 H.C. Clark and C.R. Jablonski, Inorg. Chem., 13 (1974) 2213.
4 H.C. Clark and C.S. Wong, J. Amer. Chem. Soc., 96 (1974) 7213.
5 H.C. Clark and R.J. Puddephatt, Inorg. Chem., 9 (1970) 2670.
6 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1291.
7 H.C. Clark and L.E. Manzer, J. Organometal. Chem., 59 (1973) 411.
8 L.E. Manzer, J. Chem. Soc. Dalton, (1974) 1535.
9 H.C. Clark and H. Kurosawa, Inorg. Chem., 12 (1973) 357.
10 D.W. Hart and J. Schwartz, J. Organometal. Chem., 87 (1975) C11.
11 H.C. Clark, C.R. Jablonski and K. von Werner, J. Organometal. Chem., 82 (1974) C51.
12 B.W. Davies and N.C. Payne, J. Organometal. Chem., submitted.
13 B.W. Davies and N.C. Payne, Inorg. Chem., 12 (1974) 1843.
14 J. Chatt, R.G. Guy, L.A. Duncanson and D.T. Thompson, J. Chem. Soc., (1963) 5170.
15 T. Theophanides and P.C. Kong, Can. J. Chem., 48 (1970) 1084.
16 F.R. Hartley, Angew. Chem. Int. Ed., 84 (1972) 596 and references cited therein.
17 S. Trofimenko, J. Amer. Chem. Soc., 89 (1967) 3170.
18 S. Trofimenko, Inorg. Synth., 12 (1970) 99.