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Registry No. $(n\text{-}C_4H_9)_4N[(CO)PtCl_3]$, 34964-16-4; $(n\text{-}C_4H_9)_4N[(CO)PtCl_2Br]$, 51157-48-3; $(n\text{-}C_4H_9)_4N[(CO)PtCl_2I]$, 38626-17-4; $(OC)PtCl_2(4\text{-}pyCOCH_3)$, 20064-58-8; $(OC)PtCl_2(4\text{-}pyCO_2CH_3)$, 20064-59-9; $(OC)PtCl_2(py)$, 51261-84-8; $(OC)PtCl_2(4\text{-}pyC_2H_5)$, 51157-49-4; $(OC)PtCl_2(4\text{-}pyCH_3)$, 20064-55-5; $(OC)PtCl_2[4\text{-}pyC(CH_3)_3]$, 51157-50-7; py, 110-86-1; 4-pyCH$_3$, 108-89-4.

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, N6A 3K7, Canada

Five-Coordinate Methylplatinum(II)-Acetylene Complexes Stabilized by Tridentate Poly(pyrazolyl)borate Ligands

H. C. CLARK*[1] and L. E. MANZER

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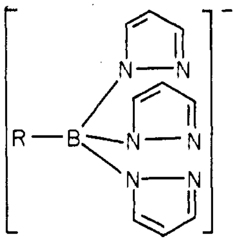
A variety of five-coordinate methylplatinum(II)–acetylene complexes stabilized by tridentate poly(pyrazolyl)borate ligands have been prepared. Nuclear magnetic resonance studies indicate that the complexes are trigonal bipyramidal with the acetylene constrained within the trigonal plane of the platinum and two equatorial pyrazolyl nitrogen atoms. Double-resonance nuclear magnetic resonance experiments have allowed assignment of all the 3-H, 4-H, and 5-H resonances of the pyrazolyl rings. The infrared C≡C stretching frequencies are discussed in relation to the bonding and chemistry of coordinated acetylenes.

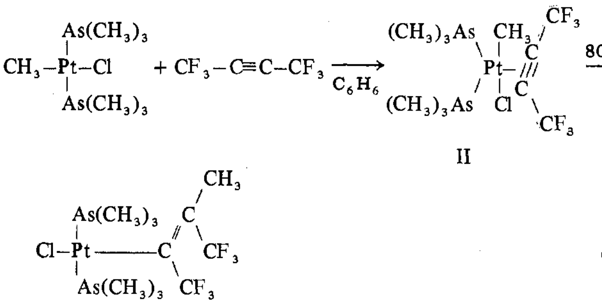
Introduction

Several years ago Trofimenko discovered a new class of ligands,[2] the poly(pyrazolyl)borate ions[3] $[R_nB(pz)_{4-n}]$, and in a number of publications,[4] the similarities between the bis(pyrazolyl)borate ions and the β-diketonate ions, as ligands, were established. The tris(pyrazolyl)borate ions, I, are unique, in being the first examples of uninegative, tridentate ligands of C_{3v} symmetry and form a number of complexes analogous to their well-known cyclopentadienyl counterparts. Although structurally similar, the tris(pyrazolyl)borate complexes are generally much more stable than the cyclopentadienyl compounds. For example, Cu(CO)[HB(pz)$_3$][5] is air and heat stable while Cu(CO)(π-C$_5$H$_5$)[6] is thermally unstable and air sensitive.



I

Five-coordinate complexes of platinum(II) are sufficiently rare[7-14] that the possibility of stabilizing such species using a tridentate poly(pyrazolyl)borate ligand was worth exploring. In particular, we were interested in the formation of five-coordinate olefin and acetylene complexes which have been postulated as intermediates in the transition metal catalyzed polymerization and hydrogenation of olefins and acetylenes[13-21]. For example, *trans*-Pt(CH$_3$)ClL$_2$ (L = tertiary phosphine, arsine, or stibine) reacts with an excess of perfluorobut-2-yne to give 1:1 adducts,[14] II (eq 1). The structure of the five-coordinate adduct, II,



(1)

has been determined by a three-dimensional X-ray analysis, confirming the trigonal-bipyramidal configuration.[22] Insertion of the platinum methyl group into the C≡C bond occurs at 80° to give the vinylplatinum(II) complex.[16]

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[1] To whom correspondence should be addressed.

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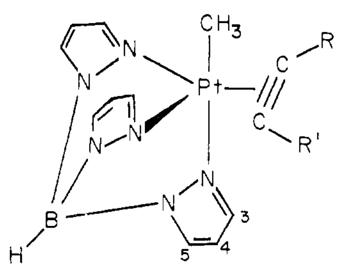
We have successfully prepared a number of five-coordinate acetylene, olefin, and allene complexes of platinum(II)[23] and in this paper discuss the synthesis, structure, and bonding of the acetylene complexes.

Results and Discussion

(a) Preparation of the Complexes. A recent study[24] of the reactions of $Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})$ has shown that the 1,5-cyclooctadiene ligand is very tightly bonded to platinum and is not easily displaced. However, if the chloride ion is removed by the silver salt of a noncoordinating anion in acetone or tetrahydrofuran with the formation of $[Pt(CH_3)(\pi\text{-}1,5\text{-}C_8H_{12})(solvent)]^+$, the cyclooctadiene is quite labile and easily displaced.[25] Hence the subsequent addition of an acetone or tetrahydrofuran solution of $K[HB(pz)_3]$ results in the displacement of 1,5-cyclooctadiene and the formation of a beige precipitate. The reaction is usually accompanied by some reduction to give metallic platinum. The exact nature of the beige precipitate is unknown. Due to its insolubility, purification by recrystallization was not possible and good analytical data could not be obtained. On the basis of its derivatives, we have assigned it the empirical formula $Pt(CH_3)[HB(pz)_3]$. In view of its low solubility the compound is probably polymeric with two pyrazolyl rings coordinated in a bidentate manner to one platinum atom with the third pyrazolyl ring bridging to fill the fourth coordination site of a second platinum atom.

Although the polymer is insoluble in dichloromethane, it readily dissolves in the presence of various acetylenes; the extent of the reaction may be monitored by dissolution of the polymer. Since the dichloromethane solutions were always colored due to contamination by platinum metal, it was always necessary to pass the solutions through a short Florisil column to remove this contaminant. The complexes were then isolated in reasonable yields and were stable both in solution and in the solid state. Most of the complexes melt sharply without elimination of the acetylene. Analytical and physical data for the acetylene complexes are given in Table I.

(b) Structure and Nuclear Magnetic Resonance Studies. On the basis of the following data we have assigned structure III to the acetylene complexes. Each pyrazolyl ring has three protons which we have labeled as 3, 4, and 5. The 3-H and 5-H resonances in the ^1H nmr spectrum appear as doublets due to coupling with the 4-H proton, and the 4-H proton appears as a triplet due to coupling with the 3- and 5-H protons. The 4-H proton resonances in the nmr spectrum are well separated from the 3-H and 5-H resonances, absorbing 1–2 ppm upfield. For the symmetrically substituted acetylenes $CH_3OOCC{\equiv}CCOOCH_3$, $C_6H_5C{\equiv}CC_6H_5$, and $CF_3C{\equiv}CCF_3$ two distinct 4-H resonances were observed in the ratio of 2:1 indicating that (a) the pyrazolylborate ligand was not fluxional on the nmr time scale and (b) two pyrazolyl rings were magnetically equivalent and different from the third ring. Each 4-H resonance is flanked by ^{195}Pt satellites ($I = {}^1/_2$, 33.8% natural abundance) and a larger ^{195}Pt coupling constant is observed to the two *equivalent* 4-H protons than to the third 4-H proton (Table II). This suggests that the group of highest nmr trans influence,[26] *i.e.*, CH_3^-, is trans to the unique pyrazolyl ring as shown in III. For the unsymmetrically substituted acetylenes, three 4-H resonances were observed, each accompanied by ^{195}Pt satellites which suggests that the acetylene is constrained within the trigonal plane and is not rotating. If the acetylenes were perpendicular to the trigonal plane, the two equatorial rings would be equivalent. The nmr evidence is therefore consistent with structure III and analogous to that of II.



III

Previously, definite assignment of the 3-H and 5-H proton resonances has not been possible; however, by utilizing the presence of the ^{195}Pt nuclear spin and by applying homonuclear double-resonance nmr techniques we have been able to make complete assignments. The nmr spectrum of the dimethyl acetylenedicarboxylate complex in the pyrazolyl ring region is shown in Figure 1(a). The two triplet resonances labeled B_1 and B_2 appear in the ratio of 2:1 and are therefore assigned to the 4-H equatorial and 4-H axial protons. Irradiation of B_1 (Figure 1(b)) caused two resonances, labeled A_1 and C_1, to collapse into singlets which indicates that the 4-H equatorial protons were spin-spin coupled to protons A_1 and C_1. Both the A_1 and C_1 proton resonances are coupled to ^{195}Pt with coupling constants of 9 and 2 Hz, respectively. We assign the resonances showing the larger coupling constant with ^{195}Pt to the 3-H protons and the other resonances to the 5-H protons, although the possibility exists that these assignments may be reversed. We therefore assign A_1 to the resonance of the equatorial 3-H protons and C_1 to the equatorial 5-H protons. Similarly, by irradiating at B_2 the resonances labeled A_2 and C_2 collapsed. There is a negligible coupling between ^{195}Pt and the proton labeled A_2 and a coupling constant of 7.0 Hz between ^{195}Pt and proton C_2. Resonances A_2 and C_2 are therefore assigned to the axial 5-H and 3-H protons, respectively. By simultaneous irradiation at B_1 and B_2 the complete 4-H decoupled spectrum may be obtained. In Figure 1(c) is shown the effect of irradiating A_1 and C_1 on the two equatorial 4-H protons, B_1. By decoupling A_1 (3-H equatorial protons) the resonance at B_1 is reduced to a doublet with complex ^{195}Pt satellites as expected for an ABX spectrum ($X = {}^{195}Pt$), and similarly by irradiating at C_1 (5-H equatorial protons) the 4-H equatorial protons give an A'BX spectrum. By simultaneously irradiating at A_1 and C_1, the resonance due to the 4-H equatorial proton is reduced to a simple BX pattern and $^4J(Pt\text{-}H)$ may easily be obtained. Similarly, by irradiation of peaks A_2 and C_2 the coupling constant $^4J(Pt\text{-}H)$ to the axial 4-H proton was obtained.

As mentioned above, the nmr spectra of several complexes containing unsymmetrically substituted acetylenes are more complicated, in that the two equatorial pyrazolyl rings are magnetically inequivalent and consequently nine resonances are expected in the region 6–8 ppm. However,

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Table I. Analytical, Physical, and Infrared Data for Five-Coordinate Acetylene Complexes $Pt(CH_3)[RB(pz)_3](ac)$

		% carbon		% hydrogen		% nitrogen				
R	Acetylene (ac)	Calcd	Found	Calcd	Found	Calcd	Found	Mp,[a] °C	Color[a]	Infrared data, cm^{-1}
pz	$CF_3C{\equiv}CCF_3$	31.37	31.37	2.32	2.24	17.20	17.41	154-156	White	$\nu(C{\equiv}C)$ 1861, 1833
pz	$C_6H_5C{\equiv}CC_6H_5$	48.62	48.29	3.78	3.67	16.80	16.71	209-211	Pale pink	$\nu(C{\equiv}C)$ 1816
pz	$CH_3O_2CC{\equiv}CCO_2CH_3$	36.17	36.87	3.36	3.25	17.75	17.51	150-152	Yellow	$\nu(CO)$ 1715, $\nu(C{\equiv}C)$ 1829
H	$CF_3C{\equiv}CF_3$	28.73	28.77	2.24	2.03	14.36	14.45	216-217	White	$\nu(B-H)$ 2495
H	$CH_3O_2CC{\equiv}CCO_2CH_3$	33.99	33.97	3.39	3.21	14.87	14.96	209-210	Yellow	$\nu(B-H)$ 2517, $\nu(CO)$ 1707, 1694
H	$C_6H_5C{\equiv}CC_6H_5$	47.93	47.63	3.86	3.72	13.97	13.76	>240[b]	Pale pink	$\nu(B-H)$ 2479
H	$CH_3C{\equiv}CC_6H_5$	42.32	42.68	3.93	3.82	15.59	15.63	139-141	Yellow	$\nu(B-H)$ 2465
H	$CH_3C{\equiv}CCO_2CH_3$	34.56	34.29	3.67	3.67	16.12	16.32	>150[b]	Pale yellow	$\nu(B-H)$ 2500, $\nu(CO)$ 1687
H	$C_6H_5C{\equiv}CCO_2CH_3$	41.18	41.46	3.63	3.60	14.41	14.22	215-217	Pale orange	$\nu(B-H)$ 2495, $\nu(CO)$ 1677
H	$HC{\equiv}CCO_2CH_3$	33.15	33.40	3.38	3.37	16.57	16.39	>250[b]	Pale yellow	$\nu(B-H)$ 2482, $\nu(CO)$ 1683
H	$HC{\equiv}CCOCH_3$	34.23	34.50	3.49	3.52	17.11	17.19	>180[b]	Pale yellow	$\nu(B-H)$, 2480, $\nu(CO)$ 1669
H	$HC{\equiv}CCF_3$	30.19	30.46	2.73	2.82	16.25	16.22	118-120	White	$\nu(B-H)$ 2485

[a] Melting points are uncorrected. [b] Darkens slowly with decomposition.

Table II. Nmr Data[a] for Five-Coordinate Platinum(II) Complexes of the Type $[RB(pz)_3]Pt(CH_3)(ac)$

		Platinum methyl		Pyrazole[b]	3-H		4-H			5-H	
R	ac	δ	^2J(Pt-H)	ring	δ	^3J(Pt-H)	δ	^4J-(Pt-H)	^3J-(H-H)	δ	Other resonances and couplings
pz	$CF_3C{\equiv}CCF_3$	1.13	66.8	eq	7.82	10.5	6.28	9.5	2.5	7.70	$\delta(CF_3)$ 56.70, $J(Pt-F) = 66.6$
				ax.	7.31	7.0	6.17	3.0	2.0	8.00	
				free[c]	7.98		6.62		2.0	8.03	
pz	$CH_3O_2CC{\equiv}CCO_2CH_3$	1.04	67.6	eq	7.88	10.5	6.40	8.0	2.0	7.66	$\delta(OCH_3)$ 3.85
				ax.	7.36	6.0	6.25	4.5	1.5	7.84	
				free[c]	7.90		6.72		1.5	7.99	
pz	$C_6H_5C{\equiv}CC_6H_5$	0.74	69.0	eq	7.93	5.5	6.37	7.5	2.0	7.48	
				ax.	7.15	8.0	5.98	3.0	2.2	7.43	
H	$CF_3C{\equiv}CCF_3$	1.06	67.4	eq	7.76	7.0	6.26	10.0	2.5	7.74	$\delta(CF_3)$ 67.40, $J(Pt-F) = 65.0$
				ax.	7.22	8.8	6.11	3.5	2.1	7.65	
H	$CH_3O_2CC{\equiv}CCO_2CH_3$	1.02	67.9	eq	7.80	9.0	6.23	10.0	2.2	7.73	$\delta(OCH_3)$ 3.84
				ax.	7.28	7.0	6.08	3.0	2.2	7.61	
H	$CH_3C{\equiv}CC_6H_5$	0.67	69.5	eq	7.74	7.0	6.24	7.5	2.0	7.72	$\delta(CH_3)$ 2.29, $J(Pt-H) = 62.6$
				eq	7.88	8.0	6.21	7.5	2.0	7.72	
				ax.	7.07	7.0	5.94	3.3	2.1	7.60	
H	$CH_3C{\equiv}CCO_2CH_3$	0.78	69.0	eq	7.84	6.5	6.22	8.0	2.5	7.72	$\delta(CH_3)$ 2.26, $J(Pt-H) = 49.0$
				ax.	7.21	7.0	6.04	4.0	2.0	7.62	$\delta(OCH_3)$ 3.70
H	$C_6H_5C{\equiv}CC_6H_5$	0.79	69.0	eq	7.94	8.0	6.32	7.5	2.0	7.77	
				ax.	7.06	7.5	5.91	4.0	2.0	7.63	
H	$C_6H_5C{\equiv}CCO_2CH_3$	0.89	69.0	eq	7.77	8.5	6.31	9.0	2.0	7.73	$\delta(OCH_3)$ 3.82
				eq			6.27	9.0	2.0		
				ax.	7.07	8.0	5.95	3.7	2.0	7.60	
H	$HC{\equiv}CCO_2CH_3$	0.85	68.6	eq	7.84	9.0	6.22	9.5	2.2	7.72	$\delta(CH)$ 4.88, $J(Pt-H) = 52.0$
				eq			6.23	10.0	2.2	7.74	$\delta(OCH_3)$ 3.74
				ax.	7.24	6.5	6.04	4.0	2.0	7.62	
H	$HC{\equiv}CC({=}O)CH_3$	0.80	68.5	eq	7.83	8.5	6.25	9.0	2.5	7.72	$\delta(CH)$ 4.93, $J(Pt-H) = 57.5$
				ax.	7.17	7.7	6.06	4.7	2.0	7.62	$\delta(COCH_3)$ 2.46, $J(Pt-H) = 5.5$
H	$HC{\equiv}CCF_3$	0.87	68.0	eq	7.76	8.0	6.21	9.0	2.0	7.75	$\delta(CH)$ 4.59 q, $J(H-F) = 3.0$, $J(Pt-H) = 50.0$
				eq			6.24	9.0	2.0		$\delta(CF_3)$ 55.4 d, $J(Pt-F) = 82.4$
				ax.	7.24	7.5	6.07	3.5	2.0	7.65	

[a] ^1H chemical shifts are reported in ppm (positive) downfield from TMS and ^{19}F chemical shifts in ppm (positive) upfield from $CFCl_3$; coupling constants are in hertz. Spectra were recorded on $CDCl_3$ solutions; q = quartet, d = doublet. [b] eq = equatorial, ax. = axial, free = uncoordinated pyrazolyl ring. [c] 3-H and 5-H protons may be interchanged.

by careful double-resonance experiments, all of the 3-H, 4-H, and 5-H resonances could be assigned (Table II). A chemical shift sequence emerges from the data as follows (in order of increasing magnetic field strength): 3-H(equatorial) < 5-H(equatorial) < 5-H(axial) < 3-H(axial) < 4-H(equatorial) < 4-H(axial). This shift sequence shows that the order of the 3-H and 5-H resonances is reversed for the equatorial and axial rings and clearly demonstrates that for other metal complexes of poly(pyrazolyl)borate ligands, where coupling constant data are lacking, it is risky to assign the 3-H and 5-H resonances from their chemical shifts alone.

The terminal acetylenic protons appear near 5 ppm downfield from TMS in the nmr spectra as illustrated in Figure 2 for the complex with $HC{\equiv}CC({=}O)CH_3$. The platinum methyl and acyl methyl resonances are shown at 0.80 and 2.46 ppm with ^{195}Pt-^1H coupling constants of 68.5 and 5.5 Hz, respectively. The acetylenic proton in the 3,3,3-trifluoropropyne complex appears as a quartet due to spin-spin coupling with the three ^{19}F nuclei and is flanked by ^{195}Pt satellites.

(c) Infrared Spectra of the Acetylene Complexes. The infrared spectra of the acetylene complexes below 1600 cm^{-1} were exceedingly complicated due to the many vibrations of the hydrotris(1-pyrazolyl)borate ligand and no attempt has been made to assign ligand or metal-ligand vibrations in this region. A fairly strong, broad band near 2500 cm^{-1} was assigned to the B-H stretching frequency. A strong and sharp band between 1700 and 1900 cm^{-1} can be assigned to the acetylenic $C{\equiv}C$ stretching frequency. These values are tabulated in Table III along with the values of $\Delta\nu(C{\equiv}C)$, which is the difference in $\nu(C{\equiv}C)$ for the free acetylene and the coordinated acetylene. Although dimethylacetylene formed an adduct with $Pt(CH_3)[HB(pz)_3]$,

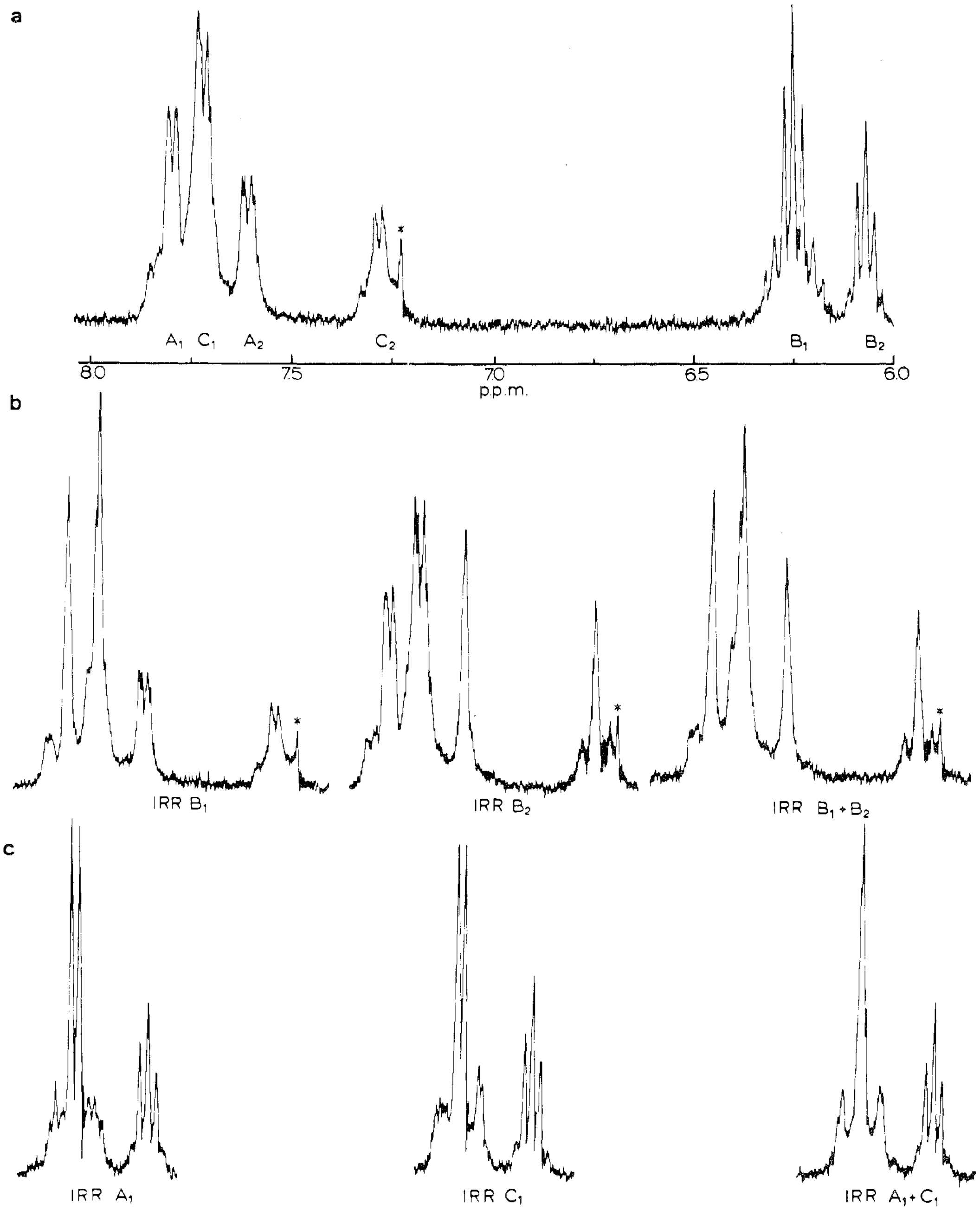


Figure 1. (a) Nmr spectrum of $Pt(CH_3)[HB(pz)_3](CH_3OOCC{\equiv}CCOOCH_3)$ in $CDCl_3$ showing the pyrazolyl ring proton resonances. The asterisk indicates $CHCl_3$ impurity. (b) Effect of irradiating at B_1 and B_2 on resonances A_1, C, A_2, and C_2. (c) Effect on B_1 of irradiating at A_1 and C_1.

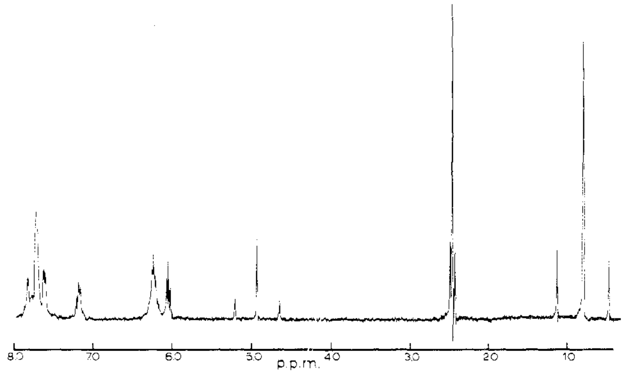


Figure 2. ^1H nmr spectrum of $Pt(CH_3)[HB(pz)_3](HC{\equiv}CC({=}O)CH_3)$ in $CDCl_3$.

Table III. $\nu(C{\equiv}C)$ for Complexes $Pt(CH_3)[HB(pz)_3](ac)$ (cm^{-1})

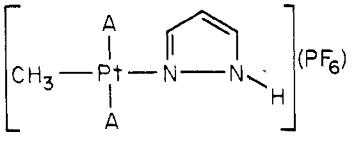
ac	$\nu(C{\equiv}C)$(complex)[a]	$\Delta\nu(C{\equiv}C)$[b]
$CF_3C{\equiv}CCF_3$	1843	457
$C_6H_5C{\equiv}CCO_2CH_3$	1801	427
$CH_3O_2CC{\equiv}CCO_2CH_3$	1823	424
$CH_3C{\equiv}CCO_2CH_3$	1835	415
$HC{\equiv}CCF_3$	1754	408
$C_6H_5C{\equiv}CC_6H_5$	1818	404
$C_6H_5C{\equiv}CCH_3$	1857	395
$HC{\equiv}CC({=}O)CH_3$	1710	388
$HC{\equiv}CCO_2CH_3$	1754	375
$CH_3C{\equiv}CCH_3$	1893	340

[a] Values are accurate to ±1 cm^{-1}, recorded on CH_2Cl_2 solutions.
[b] $\nu(C{\equiv}C)$(free acetylene) − $\nu(C{\equiv}C)$(complex).

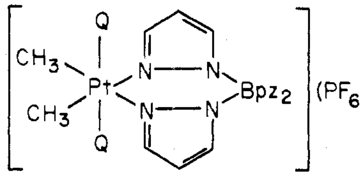
it was stable only in the presence of excess acetylene. Upon removal of the excess acetylene, the original platinum polymer was isolated. The infrared spectrum of the complex could be recorded in the presence of excess acetylene and a weak band near 1893 cm^{-1} was assigned to $\nu(C{\equiv}C)$.

It is generally accepted[27] that electron-withdrawing substituents increase the amount of π back-bonding from metal orbitals into π^*-antibonding orbitals on the acetylene resulting in a decrease in the C≡C bond order. Therefore, by comparing the values of $\Delta\nu$(C≡C) for the three series of acetylene complexes (a) RC≡CR (R = CF_3, CH_3, $COOCH_3$, C_6H_5), (b) RC≡$CCOOCH_3$ (R = C_6H_5, CH_3, H), and (c) RC≡CH (R = $COOCH_3$, $COCH_3$, CF_3), we can arrange the substituents in order of their decreasing electron-withdrawing ability: $CF_3 > C(=O)CH_3 > C(=O)OCH_3 > C_6H_5 > CH_3 > H$.

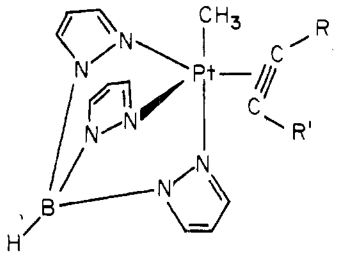
(d) Bonding. During the last few years we have accumulated data concerning the factors which affect ^2J(Pt-CH_3) for a variety of methylplatinum(II)[28] and methylplatinum(IV)[29] complexes. It is interesting to compare the values of ^2J(Pt-CH_3) for complexes IV-VI (A = As$(CH_3)_3$, Q = $P(CH_3)_2(C_6H_5)$).



IV

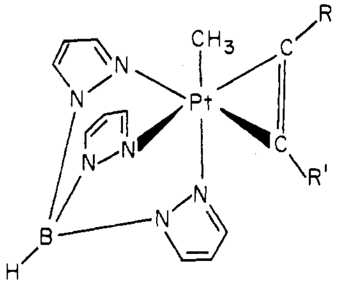


V



VI

The methylplatinum(II) complex IV was prepared by treating *trans*-Pt(CH_3)Cl[As$(CH_3)_3$]$_2$ with $AgPF_6$ and pyrazole. The dimethylplatinum(IV) compound V was prepared previously.[29] In all three complexes, a methyl group is trans to a coordinated pyrazole ring and since cis ligands have little effect on the values of ^2J(Pt-CH_3),[26] the value of this coupling constant should give some indication of the distribution of Pt 6s character within the three complexes. By comparing the values of ^2J(Pt-CH_3) for analogous complexes of platinum(II) and platinum(IV) we have previously suggested[28,29] that on oxidation the platinum-methyl bond retains 80–95% of its "6s" character. The ratio of ^2J(Pt-CH_3) for complexes IV and V, 75.4 and 64.2 Hz, respectively, is 0.85 suggesting that on oxidation, the platinum-methyl bond in these complexes retains 85% of its Pt 6s character. Therefore we would expect the value of ^2J(Pt-CH_3) for VI to lie somewhere between these two extremes. The average value of ^2J(Pt-CH_3) for all of the acetylene complexes in Table II is 68.6 Hz, very close to the average value of 68.8 Hz for IV and V. This value is therefore consistent with the formulation of the acetylene complexes as five-coordinate platinum(II) compounds and *not* six-coordinate complexes of platinum(IV), VII, formed



VII

by an oxidative addition reaction.

In Table IV, some infrared and nmr coupling constant data are tabulated for known hexafluorobut-2-yne complexes of platinum. By comparing the data for the two arsine and phosphine complexes of formally Pt(0) and Pt(II), it was suggested[14] that small differences in $\Delta\nu$(C≡C) are probably not a good criterion for deciding bond types but that the coupling constant J(Pt-F) is probably a better criterion. We believe that changes in the coupling constant data merely reflect differences in the nmr trans influences of the trans ligands (*i.e.*, distribution of Pt 6s character) and cannot be directly related to platinum-acetylene bond strengths as has been implied.[22] The similarity of the ratio of J(Pt-F)(arsine)/J(Pt-F)(phosphine) for P(0) and Pt(II) suggests that the mechanism of the coupling is independent of the formal oxidation state of the metal, the latter merely contributing to the magnitude of this coupling:[30] for J(Pt-F), Pt(0) > Pt(II). It is not surprising, therefore, that J(Pt-F) for the hydrotris(1-pyrazolyl)borate complex is larger than for the arsine- and phosphine-platinum(II) complexes, since the nmr trans influence order is $PR_3 > AsR_3 >$ pyrazole. The values of $\Delta\nu$(C≡C) for the three five-coordinate Pt(II) complexes in Table IV are *not* consistent with the greater stability of the poly(pyrazolyl)borate complex compared with the phosphine- and arsineplatinum(II) complexes. Therefore it is apparent that small variations in $\Delta\nu$(C≡C) cannot be directly related to the stability of metal-acetylene complexes.

The change in ν(C≡C) on coordination reflects a variation in the C≡C bond order which may result from both σ and π bonding. Donation of pπ electrons from the acetylene into empty platinum "d" orbitals (σ donation) will (a) *decrease* the C≡C bond order and (b) *decrease* the electron density at the acetylenic carbons. Donation of platinum "d" electrons into empty acetylene π^* orbitals (π back-bonding) will (c) *decrease* the C≡C bond order and (d) *increase* the electron density at the acetylenic carbons. The points to note are that *both* σ bonding (a) and π bonding (c) will lower ν(C≡C) while the electron density at the acetylenic carbons may differ (b and d). Such differences in acetylenic electron density may account for the differing stabilities of the poly(pyrazolyl)borate-acetylene complexes compared with the analogous phosphine and arsine complexes, even though the $\Delta\nu$(C≡C) values are essentially the same.

A further point of interest is the inertness of these hydrotris(1-pyrazolyl)borate-platinum(II)-acetylene complexes

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Table IV. Infrared and Nmr Spectroscopic Data for Some Hexafluorobut-2-yne Complexes of Platinum

Compd	ν(C≡C), cm^{-1}	$\Delta\nu$-(C≡C), cm^{-1}	J(Pt–F), Hz	Ref
$Pt[As(C_6H_5)_3]_2 \cdot C_4F_6$	1775	525	80	*a*
$Pt[P(C_6H_5)_3]_2 \cdot C_4F_6$	1775	525	65.1	*a*
$Pt(CH_3)[HBpz_3] \cdot C_4F_6$	1843	457	65.0	*b*
$Pt(CH_3)Cl[As(CH_3)_3]_2 \cdot C_4F_6$	1838	462	40	*c*
$Pt(CH_3)Cl[P(CH_3)_3]_2 \cdot C_4F_6$	1827	473	34	*c*

[a] S. Trofimenko, *J. Amer. Chem. Soc.*, 91, 3183 (1969). [b] This work. [c] Reference 14.

toward Pt–C insertion into the acetylenic bond. For insertion to occur, orbital symmetry requires the Pt–C and C≡C bonds to be coplanar. A relatively larger π component to the platinum–acetylene bond will increase the energy barrier for rotation of the olefin into the coplanar position so that insertion will be a more difficult process, consistent with our observations. Certainly an X-ray crystallographic study[31] of the hexafluorobut-2-yne complex shows that there are no steric constraints to rotation of the acetylene imposed by the hydridotris(pyrazolyl)borate ligand.

(e) **Preparation of Tetrakis(1-pyrazolyl)borate–Platinum(II)–Acetylene Complexes.** A number of tetrakis(1-pyrazolyl)borate complexes are known to be stereochemically nonrigid[32,33] so it was of interest to prepare a few complexes analogous to VI using the $[B(pz)_4]^-$ ion.

$Pt(CH_3)[B(pz)_4]$ was prepared in a manner similar to the preparation of $Pt(CH_3)[HB(pz)_3]$. It is insoluble in organic solvents and may also be polymeric. Hexafluorobut-2-yne, diphenylacetylene, and dimethyl acetylenedicarboxylate readily cleave $Pt(CH_3)[B(pz)_4]$ in dichloromethane giving crystalline 1:1 adducts. The proton nmr spectra of the hexafluorobut-2-yne and dimethyl acetylenedicarboxylate complexes were consistent with a five-coordinate structure. Three resonances in the pyrazolyl region of the nmr spectra in the ratio of 2:1:1 appeared as triplets and could thus be assigned to the 4-H protons. Only two of the three peaks showed coupling to ^{195}Pt, so the third peak was assigned to the free pyrazolyl ring. By a simple double-resonance experiment it was possible to assign all of the 3-H and 5-H protons on the coordinated pyrazolyl rings. Irradiation of the 4-H proton on the uncoordinated ring collapsed two peaks into singlets; however, due to the lack of ^{195}Pt coupling these peaks could not be unambiguously assigned to either the 3-H or 5-H protons.

The high-temperature nmr spectra (to 90°) did not show any evidence that the molecules exhibited fluxionality.

We have also attempted to prepare complexes with the $[H_2B(pz)_2]^-$ and $HB[3,5\text{-}(CH_3)_2pz]_3^-$;[34] however, these reactions were unsuccessful. Immediate reduction to platinum metal occurred with the dihydrobis(1-pyrazolyl)borate ion and the hydrotris(3,5-dimethylpyrazolyl)borate ligand appeared to degrade when added to a solution of the methyl(1,5-cyclooctadiene)platinum cation, liberating 3,5-dimethylpyrazole.

We are currently extending the range of olefins and allenes reported in the preliminary communication[23] and full details of this work will be reported in another publication.

Conclusions

1. The poly(pyrazolyl)borate ligands have been shown to stabilize five-coordinate trigonal-bipyramidal acetylene complexes of platinum(II).
2. Nmr double-resonance studies have allowed the definite assignment of all 3-H, 4-H, and 5-H proton resonances of the pyrazolyl rings and chemical shift data illustrate that it is *not* possible to assign these resonances without ancillary information such as coupling constant data.
3. The relative stabilities of closely related platinum–acetylene complexes cannot be deduced merely from values of $\Delta\nu$(C≡C). This value only reflects the summation of the components due to σ bonding and π back-bonding. The relative contributions of these individual components may govern the stability and chemistry of the coordinated acetylene.

Experimental Section

The following chemicals were obtained commercially and were used without further purification: silver hexafluorophosphate and potassium borohydride from Alfa Inorganics Inc.; pyrazole, dimethyl acetylenedicarboxylate and diphenylacetylene from Aldrich Chemical Co.; dimethylacetylene, 1-butyn-3-one, and phenylmethylacetylene from Farchan Research Laboratories; and hexafluorobut-2-yne from Peninsular ChemResearch Inc. 3,3,3-Trifluoropropyne was prepared by the method of Finegan and Norris.[35] $CH_3C{\equiv}CCO_2CH_3$,[36] $C_6H_5C{\equiv}CCO_2CH_3$,[37] and $HC{\equiv}CCO_2CH_3$[38] were prepared by Dr. K. Yasafuku according to established procedures and $Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})$ was prepared as previously described.[24] Potassium tetrakis(1-pyrazolyl)borate and potassium hydrotris(1-pyrazolyl)borate were prepared by the method of Trofimenko.[39,40]

^{1}H nuclear magnetic resonance data were recorded on a Varian Associates HA-100 spectrometer at 100 MHz using chloroform-*d* solutions and tetramethylsilane as internal lock and reference signal. ^{19}F nmr spectra were recorded on the same instrument at 94.1 MHz using $CFCl_3$ as internal reference-lock signal.

Infrared data were recorded on a Perkin-Elmer 621 grating spectrometer using Nujol mulls and dichloromethane solutions.

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

(a) **Preparation of $Pt(CH_3)[HB(pz)_3]$.** To a solution of $Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})$ (4.0 g, 1.13 mmol)[41] in 50 ml of acetone was added $AgPF_6$ (2.88 g, 1.13 mmol). The solution was stirred for 15 min and the silver chloride was removed by centrifugation to give a clear colorless solution. A solution of $K[HB(pz)_3]$ (2.75 g, 1.13 mmol) in 20 ml of acetone was added dropwise. The solution turned yellow and then dark brown, and after several minutes a precipitate formed. The solvent was removed on a rotary evaporator to give a gray-brown solid. The solid was washed with pentane, then three 50-ml portions of distilled water, 50 ml of absolute ethanol, and 50 ml of diethyl ether and air-dried. The yield was 5.27 g, mp >150°.

Anal. Calcd for $C_{10}H_{13}BN_6Pt$: C, 28.38; H, 3.10; N, 17.03. Found: C, 27.38; H, 3.11; N, 19.86.

(b) **Preparation of $Pt(CH_3)[B(pz)_4]$.** To a solution of $Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})$ (0.690 g) in 10 ml of tetrahydrofuran was added $AgPF_6$ (0.493 g) in 1 ml of THF. The solution was magnetically stirred for 10 min and the silver chloride was removed by centrifugation. $K(B(pz)_4)$ (0.620 g) in 5 ml of THF was added slowly. The solution turned yellow and then brown, and a white solid precipitated. After 30 min the solution was filtered and the solid was washed with 50 ml of distilled water, 50 ml of absolute ethanol, and 10 ml of diethyl ether. The yield was 1.35 g, mp >240°.

Anal. Calcd for $C_{13}H_{15}BN_8Pt$: C, 31.93; H, 3.09. Found: C, 33.48; H, 3.45.

(c) **Preparation of Acetylene Complexes.** A typical procedure, in the case using hexafluorobut-2-yne, is described.

$Pt(CH_3)[HB(pz)_3]$ (0.390 g) was placed in the bottom of a 20-ml thick-walled Carius tube and 5 ml of dichloromethane was added. Using standard high-vacuum techniques, a twofold excess of hexafluorobut-2-yne was condensed into the tube and the tube was sealed.

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The Carius tube was shaken for 2 hr and the solid was dissolved. The tube was opened and the solution was passed through a short 2-in. Florisil column, eluting with dichloromethane to give a clear colorless solution. The solvent was reduced in volume to about 2 ml and pentane was added to give white crystals. The flask was cooled at −14° for 12 hr; then the solvent was decanted and the crystals were dried under vacuum; yield 80%.

Analogous complexes were prepared for the other acetylenes, using essentially the same procedure except that for involatile acetylenes, it was not necessary to conduct the reaction in a sealed Carius tube. Typical yields of the complexes are as follows: dimethyl acetylenedicarboxylate, 78%; 3,3,3-trifluoropropyne, 74%; diphenylacetylene, 82%; $C_6H_5C{\equiv}CCOOCH_3$, 83%.

(d) **Preparation of *trans*-$[Pt(CH_3)\{As(CH_3)_3\}_2(N_2C_3H_4)](PF_6)$.** To a solution of *trans*-$Pt(CH_3)Cl\{As(CH_3)_3\}_2$[41] (0.204 g) in 5 ml of acetone was added 0.106 g of silver hexafluorophosphate. The precipitated silver chloride was removed by centrifuging the solution. Pyrazole (0.029 g) was added and the acetone was removed by rotary evaporation to give a clear colorless oil. The oil was dissolved in dichloromethane and ether was slowly added until the solution became cloudy. The sides of the flask were scratched with a spatula, initiating the formation of long colorless crystals. The mother liquors were decanted and the crystals were washed with ether and dried under vacuum. The yield was 88%, mp 154–156°. Nmr in $CDCl_3$: δ(Pt–CH_3) 0.43, δ(As–CH_3) 1.24, ^3J(Pt–H) = 23.0, δ(N–H) 11.34, δ(3-H) 7.63, ^3J(Pt–H) = 7.0, δ(4-H) 6.53, δ(5-H) 7.75.

Anal. Calcd for $C_{10}H_{25}As_2F_6N_2PPt$: C, 18.11; H, 3.80. Found: C, 18.03; H, 3.66.

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Registry No. $Pt(CH_3)[B(pz)_4](CF_3C{\equiv}CCF_3)$, 50932-71-3; $Pt(CH_3)[B(pz)_4](C_6H_5C{\equiv}CC_6H_5)$, 51022-65-2; $Pt(CH_3)[B(pz)_4](CH_3O_2CC{\equiv}CCO_2CH_3)$, 50859-74-0; $Pt(CH_3)[HB(pz)_3](CF_3C{\equiv}CCF_3)$, 50859-75-1; $Pt(CH_3)[HB(pz)_3](CH_3O_2CC{\equiv}CCO_2CH_3)$, 50859-76-2; $Pt(CH_3)[HB(pz)_3](C_6H_5C{\equiv}CC_6H_5)$, 50859-77-3; $Pt(CH_3)[HB(pz)_3](CH_3C{\equiv}CC_6H_5)$, 50859-78-4; $Pt(CH_3)[HB(pz)_3](CH_3C{\equiv}CCO_2CH_3)$, 50859-79-5; $Pt(CH_3)[HB(pz)_3](C_6H_5C{\equiv}CCO_2CH_3)$, 50859-80-8; $Pt(CH_3)[HB(pz)_3](HC{\equiv}CCO_2CH_3)$, 50859-81-9; $Pt(CH_3)[HB(pz)_3](HC{\equiv}CCOCH_3)$, 50932-72-4; $Pt(CH_3)[HB(pz)_3](HC{\equiv}CCF_3)$, 50859-82-0; $Pt(CH_3)[HB(pz)_3]$, 39395-33-0; $Pt(CH_3)[B(pz)_4]$, 50921-19-2; *trans*-$[Pt(CH_3)\{As(CH_3)_3\}_2(N_2C_3H_4)](PF_6)$, 50859-84-2; $Pt(CH_3)Cl(\pi\text{-}1,5\text{-}C_8H_{12})$, 50978-00-2; *trans*-$Pt(CH_3)Cl\{As(CH_3)_3\}_2$, 30179-97-6.

Contribution from the Departments of Chemistry, Indiana University, Bloomington, Indiana 47401, and Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana 46202

Metal Complexes of the Three Sparteine Diastereoisomers. Properties and Reactivities of the Copper(II) Derivatives[1a-c]

ERWIN BOSCHMANN,[1d] LEONARD M. WEINSTOCK, and MARVIN CARMACK*

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The natural alkaloid (−)-sparteine ($C_{15}H_{26}N_2$) and its two diastereoisomers, (−)-α-isosparteine and (−)-β-isosparteine, have been converted to crystalline copper(II) chloride complexes, whose properties are described. The evidence points to a tetrahedral environment about copper. Coordination with metal ions may be involved in the effect of sparteine upon muscle contraction.

Crystalline coordination compounds have been formed from copper(II) chloride and each of the three alkaloidal diastereoisomers (−)-β-isosparteine, (−)-sparteine, and (−)-α-isosparteine (Figure 1a, 1b, and 1c, respectively). Their structures and properties are described. At the time we had first isolated (−)-β-isosparteine from *Lupinus sericeus* Pursh and elucidated its structure and stereochemical relationship to the other isomers,[1b,c] we began the exploration of metal complexes derived from the sparteine stereoisomers. There had been a history of use of common (−)-sparteine as a reagent for qualitative cation analyses.[2]

Since the discovery of sparteine in 1850, the alkaloid has had a long history of use in medicine, particularly for the stimulation of muscular action in the heart,[3a] lung,[3b] and uterus.[3c,4-6] As early as 1929[7] there were indications that some of the biological actions of sparteine may result from interactions with calcium ion *in vivo*. More recently, other studies[8,9] have shown that complexes of sparteine with organometallic compounds form in solution; some of these complexes have utility in directing stereoselective syntheses.

Recent progress[10,11] in the elucidation of the role of calcium ion in muscle contractile processes have caused us to take up again[12] the study of calcium complexes as possible inter-

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* To whom correspondence should be addressed at the Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

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