and implies that, in this transition state, the bond between platinum and nitrogen is almost completely broken. This is a restatement of the conclusion of Leffler and Grunwald that a slope of 1.0 in such a relationship indicates that the transition state resembles the products of the reaction (use of $-\log K$ in this plot considers the change in the direction of amine loss and chloride gain).[20] It does not necessarily imply a dissociative intimate mechanism (except insofar as the reactive intermediate is dissociating), and in this case, the first-order dependence upon chloride ion concentration indicates clearly an A mechanism. Yet the behavior closely resembles that encountered in the aquation of the $[Co(NH_3)_5X]^{2+}$ complexes where the plot of $\log k$ against $\log K$ has a slope of 1.0;[21] in this case there is a great deal of other evidence to suggest that the intimate mechanism is essentially dissociative although the intermediate of lower coordination number may not be free enough for the assignment of a D mechanism. This is a further reminder that rate constants or equilibrium constants or any quantity that is derived from them do not provide direct evidence quantifying the molecularity of solvent participation and that an unquestioning use of LFER relationships of this sort to determine the molecularity of substitution reactions in which a molecule of the solvent is either the entering or the leaving group is dangerous and can be misleading.

Acknowledgments. R. R. acknowledges a grant from NATO and wishes to thank Professor G. Faraone for leave of absence. K_2PtCl_4 was generously loaned by Johnson, Matthey and Co. Ltd. We wish to thank Mr. P. D. Braddock for considerable assistance in this work.

Registry No. *trans*-[PtCl$_2$(DMSO)(piperidine)], 32370-20-0; *trans*-[PtCl$_2$(DMSO)(*n*-butylamine)], 51425-26-4; *trans*-[PtCl$_2$(DMSO)(morpholine)], 32458-43-8; *trans*-[PtCl$_2$(DMSO)(aniline)], 51425-27-5; *trans*-[PtCl$_2$(DMSO)(*m*-Cl-aniline)], 51425-28-6; *trans*-[PtCl$_2$(DMSO)(*p*-Cl-aniline)], 51425-29-7; *trans*-[PtCl$_2$(DMSO)(3-Br-pyridine)], 51472-50-5; *trans*-[PtCl$_2$(DMSO)(3-Cl-pyridine)], 51425-30-0; *trans*-[PtCl$_2$(DMSO)(4-CH$_3$-pyridine)], 51425-31-1; *trans*-[PtCl$_2$(DMSO)(pyridine)], 51425-32-2; *trans*-[PtCl$_2$(DMSO)(cyclohexylamine)], 51425-33-3; *trans*-[PtCl$_2$(DMSO)(cyclopropylamine)], 51425-34-4; *trans*-[PtCl$_2$(DMSO)(3,4-dimethylpyridine)], 51425-35-5; *cis*-[PtCl$_2$(DMSO)(pyridine)], 20647-45-4; *cis*-[PtCl$_2$(DMSO)(cyclohexylamine)], 50830-89-2; *cis*-[PtCl$_2$(DMSO)(cyclopropylamine)], 50830-86-9; *cis*-[PtCl$_2$(DMSO)(cyclobutylamine)], 50830-87-0; *cis*-[PtCl$_2$(DMSO)(cyclopentylamine)], 50830-88-1; *cis*-[PtCl$_2$(DMSO)(cyclohexylamine)], 50830-89-2; *cis*-[PtCl$_2$(DMSO)(cycloheptylamine)], 50830-90-5; *cis*-[PtCl$_2$(DMSO)(cyclooctylamine)], 50830-91-6; K[PtCl$_3$(DMSO)], 31168-86-2; piperidine, 110-89-4; *n*-butylamine, 109-73-9; cyclohexylamine, 108-91-8; cyclopropylamine, 765-30-0; morpholine, 110-91-8; 3,4-dimethylpyridine, 583-58-4; 4-methylpyridine, 108-89-4; pyridine, 110-86-1; aniline, 62-53-3; 4-chloroaniline, 106-47-8; 3-chloroaniline, 108-42-9; 3-chloropyridine, 626-60-8; 3-bromopyridine, 626-55-1; chlorine, 7782-50-5.

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

Stabilization of Five-Coordinate Platinum(II) Olefin and Allene Complexes by the Hydrotris(1-pyrazolyl)borate Ligand

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

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The hydrotris(1-pyrazolyl)borate ligand has been shown to stablize five-coordinate olefin, allene, and carbonyl complexes of platinum(II). Nuclear magnetic resonance measurements suggest a trigonal-bipyramidal configuration with the olefin and allene contained within the trigonal plane of the platinum and two equatorial nitrogen atoms. When more than one geometrical isomer is possible for the olefin complexes, the ratio of isomers is dependent upon the steric requirements of the olefin substituents. An unusual hydrogen–fluorine through-space coupling interaction has been observed between the platinum methyl hydrogens or the axial pyrazolyl 3-H proton and the fluorine atoms on several fluoroolefin complexes. The olefin and allene complexes are stereochemically rigid at room temperature while the carbonyl complexes are fluxional.

Introduction

Poly(pyrazolyl)borate ligands have been shown to confer considerable stability on organometallic complexes[2-5] apparently because of the favorable electronic and geometrical properties of the ligand. For example, five-coordinate acetylene complexes of platinum(II) are relatively unstable with respect to insertion and dissociation;[6-7] however, by using the poly(1-pyrazolyl)borate ligands we have been able to stabilize a number of five-coordinate methylplatinum(II) acetylene complexes 1, where R and R′ are either electron-donating or electron-withdrawing substituents. The acetylene is constrained within the trigonal plane of the platinum

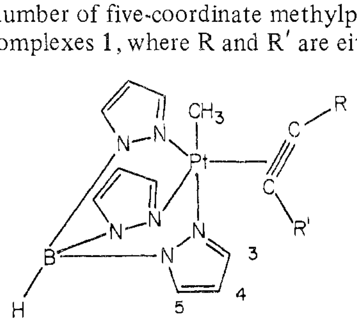

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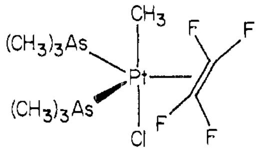
Table I. Analytical, Physical, and Infrared Data for the Five-Coordinate Complexes $Pt(CH_3)[HB(pz)_3](un)$

un	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found	% nitrogen Calcd	% nitrogen Found	Mp,[a] °C	Infrared data,[b] cm^{-1}
$CF_2=CF_2$	27.54	27.99	2.50	2.35	16.06	16.29	197-199	ν(B-H) 2531
$CH=CHCOOCO$	32.22	31.95	2.90	2.71	16.11	15.53	236-238	ν(B-H) 2489, ν(CO) 1827, 1760
cis-$(CH_3)O_2CCH=CHCO_2(CH_3)$	33.87	33.87	3.73	3.55	14.82	14.81	202-204	ν(B-H) 2482, ν(CO) 1753 sh, 1744 s, 1726 sh
trans-$(C_2H_5)O_2CCH=CHCO_2(C_2H_5)$	36.31	36.30	4.23	4.10	14.12	14.34	136-137	ν(B-H) 2494, ν(CO) 1713, 1696
p-OC_6H_4O	36.17	35.98	3.23	3.06	15.82	15.82	>220	ν(B-H) 2487, ν(CO) 1653 b
$CH_2=CHCO_2(CH_3)$	33.01	33.30	3.76	3.70	16.50	16.70	168-169	ν(B-H) 2492, ν(CO) 1719
$CH_2=CH(CN)$	32.78	33.22	3.39	3.66	20.59	19.97	103-105	ν(B-H) 2489, ν(CN) 2223
trans-$(CH_3)CH=CH(CHO)$	34.08	34.66	3.88	3.96	17.04	16.71	135-140	ν(B-H) 2480, ν(CO) 1680
$CH_2=C(CF_3)(CN)$	30.90	30.93	2.78	2.76	18.02	17.99	150-153	ν(B-H) 2494, ν(CN) 2235
$CH_2=C(CH_3)(CN)$	34.29	34.48	3.70	3.82	20.00	20.00	>180	ν(B-H) 2487, ν(CN) 2216
$(CH_3)_2C=C=C(CH_3)_2$	39.31	39.71	4.85	4.85	16.18	15.71	101-103	ν(B-H) 2472, ν(C=C=C) ~1720 b
$(CH_3)_2C=C=CH_2$	36.67	36.93	4.31	4.07	17.11	17.10	191-192	ν(B-H) 2483, ν(C=C=C) ~1730 b
$(CH_3)CH=C=CH_2$	35.23	35.68	4.01	3.94	17.61	17.61	125-130	ν(B-H) 2480
$CF_2C=CH_2$	29.58	29.87	3.10	2.89	17.25	17.29	149-150	ν(B-H) 2500
$CF_2C=CFH$	28.53	28.66	4.01	2.60	16.64	16.64	125-130	ν(B-H) 2515

[a] Melting points are uncorrected. [b] Key: s, strong; sh, shoulder; b, broad.

and two equatorial nitrogen atoms and is surprisingly stable with respect to dissociation and insertion.

Although a large number of olefin complexes of Pt(II) and Pt(0) are known, there is only one such *five*-coordinate platinum(II) olefin complex,[7] **2**, and this readily undergoes insertion involving the platinum-methyl and C=C bonds. In the absence of excess tetrafluoroethylene the complex dissociates.



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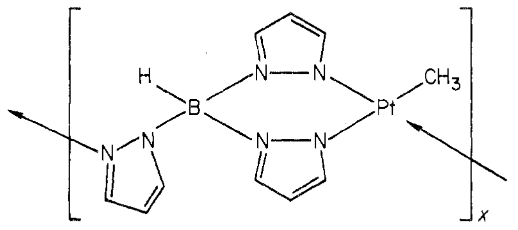
We were therefore interested in the possibility of stabilizing five-coordinate olefin and allene complexes of Pt(II).

Results and Discussion

(a) **Preparation of the Complexes.** We have recently described[5] the preparation of $Pt(CH_3)[HB(pz)_3]$ which we believe to be a polymeric compound **3** involving a bridging hydrotris(1-pyrazolyl)borate ligand. Although the complex is fairly insoluble it does dissolve in a dichloromethane solution within a period of 50-60 min in the presence of a variety of olefins forming stable 1:1 adducts. Due to contamination of **3** by platinum metal (formed during the preparation of **3**) it was always necessary to purify the complexes by passing the dichloromethane solutions through a short Florisil column. This removed all of the colored impurities giving clear, colorless solutions from which the 1:1 adducts could easily be isolated. The complexes were quite soluble in organic solvents and their nuclear magnetic resonance spectra were recorded in chloroform-*d* solutions. Analytical, physical, and infrared data are listed in Table I.



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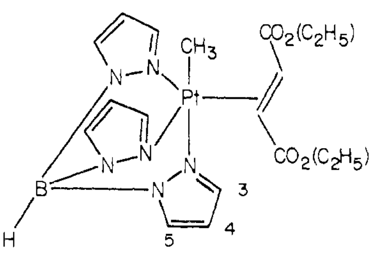
(b) **Nuclear Magnetic Resonance Studies.** The hydrogens on the pyrazolyl rings absorb in the region δ 8-6 and much of the structural information comes from a close examination of the nuclear magnetic resonance spectra in this region. The 4-H resonances for the dimethyl maleate and maleic anhydride complexes appear as triplets due to coupling with the 3-H and 5-H protons and appear well upfield (1-2 ppm) from these latter resonances; also each 4-H resonance is flanked by ^{195}Pt satellites ($I = {}^1/_2$, 33.8% natural abundance) confirming the tridentate nature of the ligand. The observance of two 4-H resonances in the ratio of 2:1 confirms the equivalence of two pyrazolyl rings which are different from the third ring. The platinum methyl resonance appears as a singlet with ^2J(Pt-H) = 66-67 Hz, indicative of a platinum methyl group trans to a pyrazolyl ring.[5] The olefinic CH resonances for these two complexes appear as singlets with fairly large ^{195}Pt satellites, (J(Pt-H) = 80-82 Hz, Table II). The presence of only one CH resonance and one carbomethoxy resonance for the dimethyl maleate complex indicates that there is a plane of symmetry perpendicular to the olefinic plane and that either (i) the C=C bond is constrained within the trigonal plane defined by the platinum and two equatorial nitrogen atoms or (ii) the olefin is rotating about the platinum-olefin bond. In order to resolve this problem we have prepared the diethyl fumarate (*trans*-$C_2H_5O_2CCH=CHCO_2C_2H_5$) complex. The nmr spectrum of this complex in the region 6-8 ppm is shown in Figure 1. Clearly, three 4-H resonances are observed at δ 6.26, 6.21, and 6.09, each accompanied by ^{195}Pt satellites. This is consistent with (but does not in itself establish) structure **4**, analogous to those observed for acetylene complexes.[5] Nonequivalence of the two equatorial rings confirms that the C=C bond is constrained within the trigonal plane and is not rotating.



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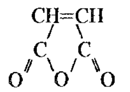
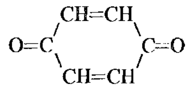
By selectively decoupling the 4-H resonances of the equatorial and axial rings it is possible to assign all 3-H, 4-H, and

Table II. ^1H Nmr Data[a] for the Five-Coordinate Complexes $Pt(CH_3)[HB(pz)_3](un)$

un	Platinum methyl		Pyrazole ring[b]	3-H		4-H			5-H	Other resonances and couplings
	$\delta(Pt-CH_3)$	$^2J(Pt-H)$, Hz		δ	$J(Pt-H)$, Hz	δ	$J(H-H)$, Hz	$J(Pt-H)$, Hz	δ	
$CF_2=CF_2$	1.17 t	71.5	eq	7.63	7.5	6.22	2.2	8.0	7.66	$Pt-CH_3$, $J(H-F) = 2.0$ t
			ax	7.55		6.12	2.5	5.0	7.61	3-H (ax), $J(H-F) = 2.0$ t
$CF_2=CH_2$	0.94 d	69.5	eq	7.68	6.0	6.16	2.0	10.0	7.67	$Pt-CH_3$, $J(H-F) = 2.0$ d
			eq			6.14	2.0	10.0		$\delta(CH_2) \sim 1.1$
			ax	7.38	4.0	6.06	2.5	4.0	7.63	3-H (ax), $J(H-F) = 2.5$ d
	0.95	65.6	eq	7.02	8.0	6.29	2.0	10.0	7.76	$\delta(CH)$ 4.13, $J(Pt-H) = 80.6$
			ax	7.08	5.5	6.27	2.0	4.5	7.74	
cis-$(CH_3)O_2CCH=CHCO_2(CH_3)$	0.97	67.3	eq	7.76	9.0	6.26	2.0	9.0	7.73	$\delta(CH)$ 3.76, $J(Pt-H) = 81.7$
			ax	7.10	5.5	6.19	2.0	4.5	7.68	$\delta(OCH_3)$ 3.80
trans-$C_2H_5O_2CCH=CHCO_2C_2H_5$	0.95	66.0	eq	7.73	8.0	6.26	2.0	9.0	7.75	$\delta(CH_3)$ 0.89, 1.30
			eq	7.50	8.5	6.21	2.5	10.0	7.71	$\delta(CH_2)$ 3.88, 4.21, $J(H-H) = 7.0$
			ax	7.87	4.5	6.09	2.5	4.5	7.61	
	0.90	67.0	eq	7.51	8.0	6.24	2.0	10.4	7.72	$\delta(CH)$ 4.41, $J(Pt-H) = 81.4$
			ax	7.10	5.5	6.21	2.0	4.0	7.69	$\delta(CH)$ 6.54
$CH_2=C=C(CH_3)_2$	0.60	68.0	eq	7.77	7.0	6.19	2.0	8.0	7.68	$\delta(C-CH_3)$ 1.78, $J(Pt-H) = 11.5$
			eq			6.18	2.0	8.0	7.67	$\delta(C-CH_3)$ 2.08, $J(Pt-H) < 1.0$
			ax	7.00	7.5	6.05	2.2	4.5	7.62	
$(CH_3)_2C=C=C(CH_3)_2$	0.70	72.0		7.60		6.02	2.0		7.34	$\delta(CH_3)$ 1.07, $J(Pt-H) = 70.0$
				7.60		6.10	2.0		7.65	$\delta(CH_3)$ 1.26, $J(Pt-H) = 52.5$
				7.72		6.22	2.0		7.68	$\delta(CH_3)$ 1.82, $J(Pt-H) = 8.5$
										$\delta(CH_3)$ 2.03, $J(Pt-H) = 2.5$
trans-$CH_3CH=CHCHO$	0.93	67.0		[c]		[c]			[c]	$\delta(CHO)$ 9.52, $J(Pt-H) = 2.0$, $J(H-H) = 5.0$
	0.92	67.0								$\delta(CH_3)$ 1.36, $J(Pt-H) = 46.0$, $J(H-H) = 6.0$
										$\delta(CH_3)$ 1.35, $J(Pt-H) = 37.5$, $J(H-H) = 6.5$
$CH_2=C(CH_3)CN$	1.07	66.0		[c]		[c]			[c]	$\delta(CH_3)$ 1.57, $J(Pt-H) = 44.0$
	0.77	67.0								$\delta(CH_3)$ 1.47, $J(Pt-H) = 55.9$
										$\delta(CH) \sim 2.5$ m
$CH_2=C(CF_3)CN$	1.02 q	66.5		[c]		[c]			[c]	$Pt-CH$, $J(H-F)$ 3.0 q
	1.18	64.5								$\delta(CF_3)$ 57.9, $J(H-F) = 1.4, 3.0$
										$J(Pt-F) = 66.0$, $\delta(CH) \sim 2.9$
$CH_2=CHCO_2(CH_3)$	0.82	66.0		[c]		[c]			[c]	$\delta(OCH_3)$ 3.46, 3.04
	0.68	66.0								
$CH_2=CH(CN)$	1.00	64.0		[c]		[c]			[c]	
	0.71	64.0								
$CF_2=CFH$	0.83 d	69.5		[c]		[c]			[c]	$Pt-CH_3$, $J(H-F) = 2.0$ d
	1.13 dd	71.5								$Pt-CH_3$, $J(H-F) = 2.0, 2.5$ dd
$CH_3CH=C=CH$	0.82	68.0		[c]		[c]			[c]	
	0.92	68.0								

[a] ^1H chemical shifts are reported in ppm (positive) downfield from $Si(CH_3)_4$ and ^{19}F chemical shifts in ppm upfield from $CFCl_3$. Spectra were recorded on $CDCl_3$ solutions. Key: m, multiplet; d, doublet; dd, doublet of doublets; q, quartet; t, triplet. [b] eq = equatorial; ax = axial. [c] Due to the presence of two isomers, these resonances were complex and could not be assigned with certainty.

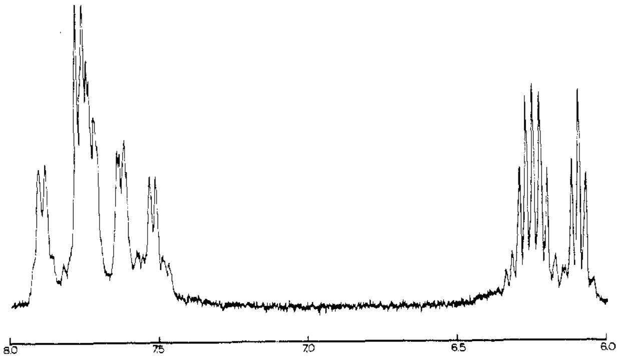
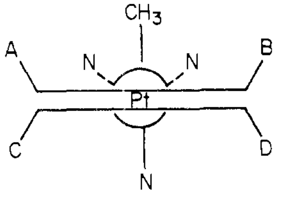


Figure 1. ^{1}H nmr spectrum of $Pt(CH_3)[HB(pz)_3][$*trans*-$(C_2H_5)O_2CCH{=}CHCO_2(C_2H_5)]$ in the region 6-8 ppm showing the pyrazolyl ring protons.

5-H resonances of all the pyrazolyl rings. These resonances are listed in Table II. A detailed description of these double-resonance experiments is outlined in the previous paper on the acetylene complexes[5] and will not be described in detail here. For the symmetrically substituted olefins, where the equatorial pyrazolyl rings are equivalent, only six resonances were observed in the region 6-8 ppm; and for the unsymmetrically substituted olefins, where the equatorial pyrazolyl rings are nonequivalent, it was possible to assign all nine proton resonances in this region of the spectrum.

Unlike the acetylene complexes, **1**, where the substituents are coplanar with the PtN_2C_2 plane, the intrinsic bonding properties of the olefins require that the plane defined by the four olefinic substituents lie approximately perpendicular to both the trigonal and axial planes of the complex. Consequently for the two 1,2-cis-disubstituted olefins, dimethyl maleate and maleic anhydride, two geometrical isomers, **5** and **6**, are possible. The olefinic substituents, R, may orient themselves toward either the platinum methyl group, **5**, or the axial pyrazolyl rings, **6**. The nmr spectra of these complexes showed that only one isomer was present.



5, A = B = olefinic substituent, C = D = H
6, A = B = H, C = D = olefinic substituent
7, A = H, B = CH_3, C = H, D = CN
8, A = H, B = CN, C = H, D = CH_3

The reaction of $Pt(CH_3)[HB(pz)_3]$, **3**, with *p*-benzoquinone gave a bright yellow complex whose nmr spectrum showed the presence of only one isomer. Two resonances could be assigned to the olefin; the hydrogens of the uncoordinated double bond appeared at δ 6.54, while the hydrogens of the coordinated double bond were considerably more shielded, absorbing at δ 4.41 and showing a large coupling constant to ^{195}Pt (*J*(Pt-H) = 81.7 Hz).

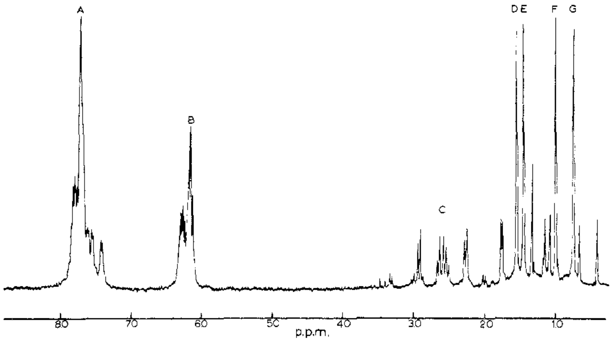
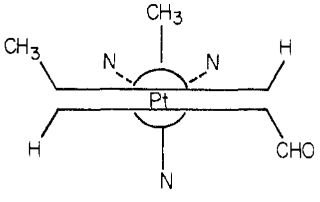


Figure 2. ^{1}H nmr spectrum of $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CN)(CH_3)]$ showing the presence of two geometrical isomers in the ratio 1:1.

The reaction between $Pt(CH_3)[HB(pz)_3]$ and methacrylonitrile ($CH_2{=}C(CH_3)(CN)$) gave a solid whose nmr spectrum (Figure 2) shows the presence of two isomers, **7** and **8**. Two platinum-methyl resonances (Figure 2F and G) are observed, each accompanied by ^{195}Pt satellites, ^2J(Pt-H) = 66.0 and 67.0 Hz, respectively. The pyrazolyl proton region is very complex due to nonequivalence of the two equatorial rings since 18 proton resonances are expected for the two isomers. No attempt was made to assign these resonances, but, as usual, the 4-H resonances (Figure 2B) are to high field of the 3-H and 5-H resonances (Figure 2A). The terminal proton ($=CH_2$) resonances appear as two overlapping ABX patterns (X = ^{195}Pt) centered near δ 2.5 (Figure 2C); however, due to the complexity of these resonances, no attempt was made to extract platinum-195 coupling constants. Two olefin-methyl resonances (Figure 2D and E) are observed, and it is interesting that the coupling constant between ^{195}Pt and the methyl hydrogens is substantially different for each isomer (*J*(Pt-H) = 44.0 and 55.9 Hz, respectively). Lewis, *et al.*,[8] observed a similar effect for the complex $PtCl(acac)(CH_3CH{=}CH_2)$, where the coupling constants between ^{195}Pt and the two terminal protons on propene were 67.2 and 77 Hz. This difference was attributed to a slight rotation of the olefin about the C=C bond due to steric interaction between the propene methyl group and the other ligands. The terminal hydrogen with the largest coupling constant was assigned to the proton nearest platinum. A similar argument for the complex $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CH_3)(CN)]$ would imply a steric interaction between either the olefin methyl or olefin cyano group and either the platinum methyl or axial 3-H proton. At this time we are unable to say which isomer, **7** or **8**, has the greater coupling constant between the olefin methyl hydrogens and platinum-195.



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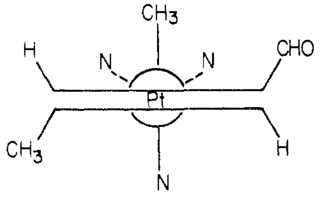

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Crotonaldehyde (*trans*-$CH_3CH{=}CH(CHO)$) reacts with $Pt(CH_3)[HB(pz)_3]$ to give a complex whose nmr spectrum shows the presence of the expected two geometric isomers, **9** and **10**, in the ratio of 1:1. The aldehyde proton appears at δ 9.52 in the nmr spectrum as a doublet due to coupling with the vicinal olefinic hydrogen (^3J(H-H) = 5.0 Hz) and is flanked by satellites due to coupling with ^{195}Pt (*J*(Pt-H) = 2.0 Hz). Two platinum-methyl resonances are observed, each with a coupling constant to ^{195}Pt of 67.0 Hz. Two resonances may also be assigned to the olefinic methyl groups, which appear as doublets due to coupling with the vicinal olefinic hydrogen (^3J(H-H) = 6-7 Hz). As observed in complexes **9** and **10**, the coupling constants *J*(Pt-H) for the

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(8) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1653 (1970).

crotonaldehyde methyl groups differ for the two isomers (37.5 and 46.0 Hz), indicating a possible twisting of the olefin about the C=C bond. No attempt was made to interpret the olefinic hydrogen resonances since they were exceedingly complex.

Acrylonitrile ($CH_2=CHCN$) reacted with $Pt(CH_3)[HB(pz)_3]$ to give a 1:1 adduct whose nmr spectrum shows the presence, once again, of two geometrical isomers in the ratio of 1:1. The nmr spectrum of the methyl acrylate ($CH_2=CHCO_2CH_3$) complex shows the presence of two isomers in the approximate ratio of 2:1. The possibility exists that this ratio of isomers is not the most thermodynamically stable one and that some of one isomer has been lost during the work-up procedure. Accordingly, the nmr spectrum of $Pt(CH_3)[HB(pz)_3](CH_2=CHCO_2CH_3)$ was observed as the temperature was raised to 150° in the hope that equilibration of the two isomers would occur. Those spectra are shown in Figure 3. The presence of two isomers may easily be seen from the 30° spectrum which shows two platinum methyl (δ 0–1.0) and two CO_2CH_3 (δ 3–4) resonances. As the temperature is raised, the former coalesce (120°) to a single broad peak and then sharpen at 150°. The carbomethoxy resonances coalesce at 150°. We originally suggested[4] that the fluxionality associated with the pyrazolyl ring protons was due to rotation of the three rings about the C_{3v} axis of the ligand. If so, changing the olefin would not likely affect this rotation. We therefore examined the high-temperature nmr spectra of the *p*-benzoquinone and maleic anhydride complexes and observed no temperature dependence up to 120° for resonances attributable to the pyrazolyl rings. The observed "fluxionality" in the methyl acrylate complex is more likely due to a coalescence of the 3-H, 4-H, and 5-H resonances due to equilibration of the two isomers and *not* to a rotation of the ligand. The mechanism by which the two isomers equilibrate may involve either (a) rotation of the olefin about the platinum–olefin bond or (b) dissociation and association of the olefin. Although a distinction between these mechanisms should be possible based on the presence or absence of ^{195}Pt coupling to the olefin protons, the complexity and quality of the nmr spectra prevent us from making this distinction. The important point to be made from these variable-temperature nmr spectra is that on cooling to 30° the same ratio of isomers exists which indicates that there is a preferred geometrical isomer. We believe these observed ratios of isomers may be explained on steric grounds.

For the two 1,1- and 1,2-trans-disubstituted olefins, crotonaldehyde and methacrylonitrile, two geometrical isomers were observed in the ratio of 1:1. However, the nmr data can be interpreted in terms of a slight twisting of the olefin due to steric interaction between one of the substituents and either the platinum methyl group or the axial pyrazolyl ring. The observed ratio of isomers indicates that there is insufficient difference in the size of the two substituents to cause the preference for one isomer over the other. Only one isomer is obtained for the three cis-disubstituted ethylenes, maleic anhydride, dimethyl maleate, and *p*-benzoquinone, presumably due to the large difference in the steric effects between the two hydrogens on one side of the C=C bond compared with the two organic substituents on the other side. Therefore by using monosubstituted olefins, $CH_2=CHR$, in which the size of R varies, one should, in principle, be able to obtain a mixture of geometrical isomers with the ratio of these isomers forming a continuum from 1:1 (where $R \approx H$) to 1:0 (where $R >>> H$). When R = CN, both isomers were obtained in the ratio of 1:1; however, when the size of R was increased to CO_2CH_3, the ratio was 1:0.5 consistent with an effect due to steric crowding. Without a crystal structure of one of the complexes we are unable to say whether it is the platinum methyl group or the axial pyrazolyl ring which affords the greater steric interaction with the olefinic substituents.

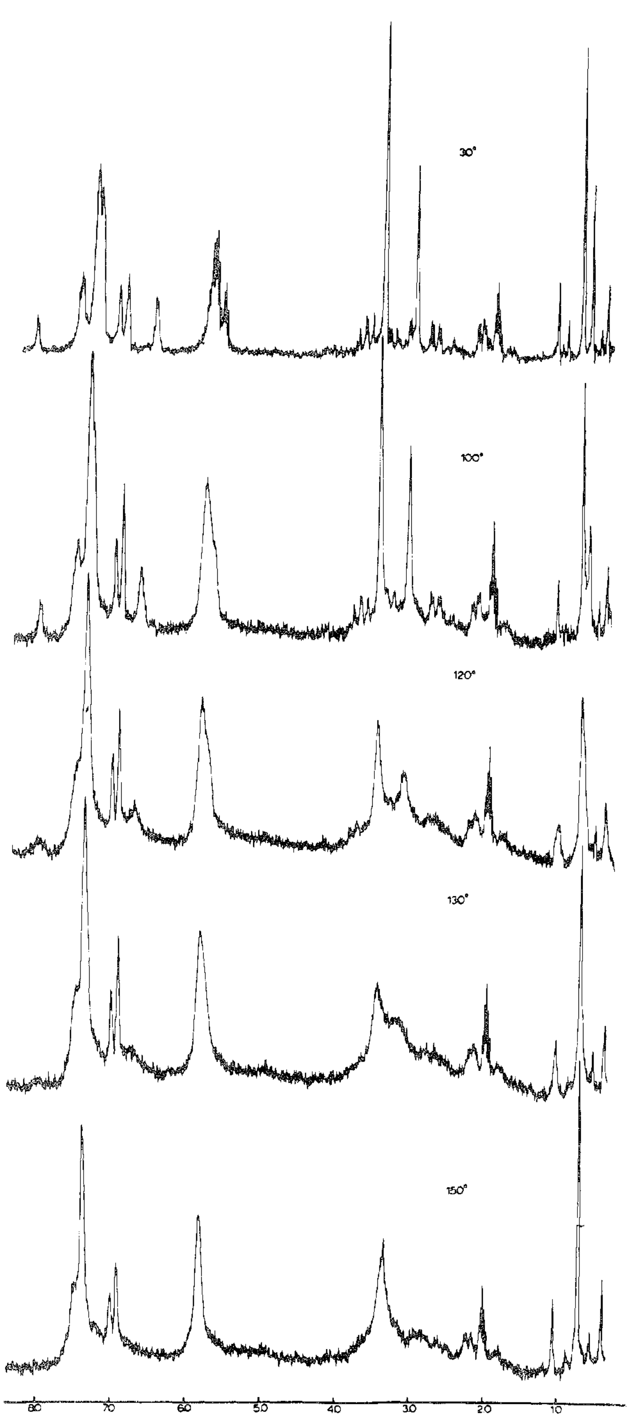


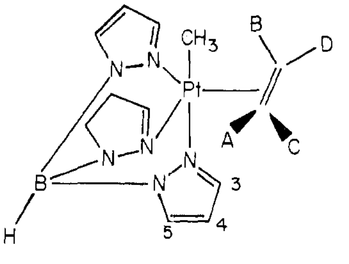
Figure 3. Variable-temperature ^1H nmr spectra of $Pt(CH_3)[HB(pz)_3][CH_2=CHCO_2(CH_3)]$ in toluene-d_8. Solvent impurities are seen near 7 and 2 ppm and are temperature independent.

Aldehyde and ketonic functional groups may exist in an enol–keto tautomeric mixture. Even though this equilibrium lies far to the left, it is reasonable to consider stabilizing the vinyl alcohol by coordination to $Pt(CH_3)[HB(pz)_3]$. However, after magnetically stirring a solution of **3** with a large excess of acetaldehyde in dichloromethane only an insoluble gum was obtained which may be polymerized olefin. No reaction occurred between $Pt(CH_3)[HB(pz)_3]$ and acetylacetone (where the enol form is present in ~80%[9]) after several days.

No reaction occurred between $Pt(CH_3)[HB(pz)_3]$ and $Cl_2C{=}CCl_2$, $CH_2{=}C(C_6H_5)_2$, or *trans*-$(C_6H_5)CH{=}CH(C_6H_5)$, presumably as a result of steric interactions.

(c) **Fluoroolefin Complexes.** In general the reactivity of coordinated olefin- and acetyleneplatinum complexes toward insertion increases as the electronegativity of the substituents increases so we have prepared several fluoroolefin complexes.

The nmr spectrum of the tetrafluoroethylene complex, **11**, was particularly interesting in that the platinum methyl resonance appeared as a 1:2:1 triplet (Figure 4b) due to coupling with only two of the fluorine atoms (J(H-F) = 2.0 Hz) and this resonance is flanked by ^{195}Pt satellites (^2J(Pt-H) = 71.5 Hz). The 3-H axial resonance in $CDCl_3$ was buried; however, in C_6D_6 the resonance was considerably deshielded, and, with the 4-H axial proton decoupled, it appeared as a 1:2:1 triplet due to coupling with only two fluorine nuclei (J(H-F) = 2.0 Hz).



11, A = F_1, B = F_2, C = F_3, D = F_4
12a, A = F, B = H, C = F, D = F
12b, A = F, B = F, C = H, D = F
13a, A = H, B = CN, C = CF_3, D = H
13b, A = H, B = CF_3, C = CN, D = H

Most electron-coupled spin-spin interactions between two nuclei are dominated by the Fermi contact mechanism;[10] however, in certain instances where two nuclei are very close together a "through-space" coupling may also be observed.[11] Examples of through-space couplings in organometallic chemistry are rare[12,13] and are only observed when one of the two nuclei has a nonbonding pair of electrons which can interact with the second nucleus (*e.g.*, ^{19}F, ^{199}Hg, ^{31}P). The above results suggested that a through-space mechanism was operative here so we have prepared several analogous fluoroolefin complexes and closely examined their nmr spectra.

The platinum methyl resonance (Figure 4a) and axial 3-H resonance of the 1,1-difluoroethylene complex appeared as 1:1 doublets due to coupling with only one fluorine atom (J(H-F) = 2.0 and 2.5 Hz, respectively).

The nmr spectrum of the trifluoroethylene complex, **12**, indicated that both geometrical isomers were obtained. Two platinum methyl resonances were observed. The first appeared as a 1:1 doublet (J(H-F) = 2.0 Hz) and the second appeared as a 1:1:1:1 doublet of doublets due to coupling of the methyl hydrogens with the two nonequivalent fluorine atoms (J(H-F) = 2.0, 2.5 Hz). We can therefore assign these resonances to complexes **12a** and **12b**, respectively. Finally, we have prepared a complex with trifluoromethacrylonitrile ($CH_2{=}C(CF_3)(CN)$). The nmr spectrum as expected showed the presence of two geometrical isomers **13a** and **13b**. The platinum methyl resonance of one isomer appeared as a singlet flanked by ^{195}Pt satellites (^2J(Pt-H) = 64.5 Hz) whereas the resonance of the second isomer appeared as a quartet due to coupling between the methyl hydrogens and the three fluorines on the CF_3 group (J(H-F) = 3.0 Hz) and the resonance is accompanied by ^{195}Pt satellites (^2J(Pt-H) = 66.5 Hz) which also appear as quartets. We assign these resonances to complexes **13a** and **13b**, respectively. The fact that the coupling between the methyl hydrogens and olefinic fluorines in **13b** is greater than in the other fluoroolefin complexes provides further support for a through-space coupling interaction. A smaller coupling constant would be predicted if the interaction involved a long-range through-bond mechanism.

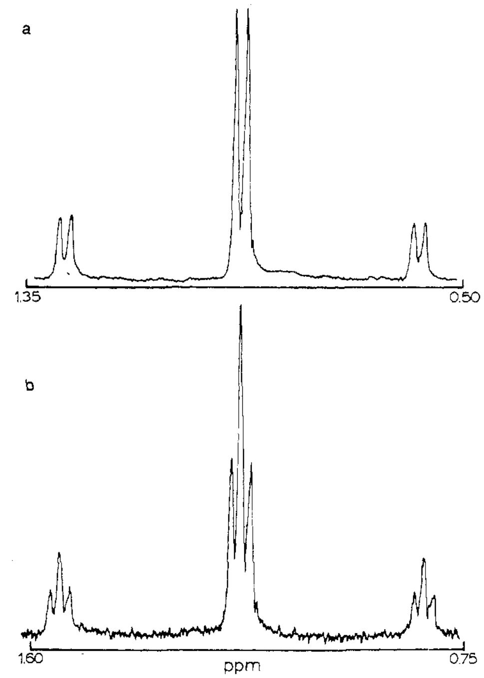


Figure 4. (a) Platinum methyl resonance in the ^{1}H nmr spectrum of $Pt(CH_3)[HB(pz)_3](CF_2{=}CH_2)$. (b) Platinum methyl resonance in the ^{1}H nmr spectrum of $Pt(CH_3)[HB(pz)_3](CF_2{=}CF_2)$.

This conclusion is also strongly supported by data obtained from ^{19}F nmr spectra. For the tetrafluoroethylene complex (**11**), a complicated AA′BB′X spectrum was observed, ignoring the proton coupling. Two sets of resonances of equal intensity are observed centered at 132 (AA′) and 121 ppm (BB′) upfield from $CFCl_3$. All of the lines in the 132-ppm resonances appear as quartets which in the heteronuclear double-resonance experiment $^{19}F\{^1H\}$ collapse into singlets. This confirms that these two fluorines are coupled to three protons, so that these resonances can be assigned to F_1 and F_2. The value of J(H-F) is 2.0 Hz and of J(Pt-F) is 325 Hz. Similarly, all of the lines in the resonances centered at 121 ppm appeared as doublets and in the proton-decoupled ^{19}F spectrum collapsed into singlets. Thus, these two fluorines (F_3 and F_4) are coupled to one proton, 3-H axial. The value of J(H-F) is 2 Hz and of J(Pt-F) is 185 Hz. Note that F_1 and F_2 have a much larger value for J(Pt-F) than F_3 and F_4.

Similarly, for the 1,1′-difluoroethylene complex, a complicated ^{19}F spectrum is observed with two sets of resonances at 106 and 95 ppm. Quartet splitting could be distinguished in the 106-ppm resonances and fine doublet splitting in the

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(9) R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966, p 943.

(10) N. F. Ramsey and E. M. Purcell, *Phys. Rev.*, **85**, 143 (1952); N. F. Ramsey, *ibid.*, 303 (1953); J. A. Pople, *Mol. Phys.*, **1**, 216 (1958); M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(11) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

(12) W. McFarlane, *Chem. Commun.*, 609 (1971).

(13) G. R. Miller, A. W. Yankowsky, and S. O. Grim, *J. Chem. Phys.*, **51**, 3185 (1969).

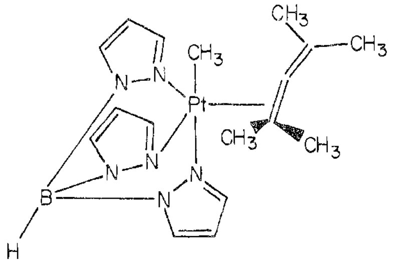
95-ppm resonance. The proton-decoupled spectrum showed only two sets of doublets with ^{195}Pt satellites, the doublet pattern arising from F_1-F_2 spin-spin coupling. Thus, the 106-ppm resonances are assigned to F_1 with J(Pt-F_1) = 280 Hz, and the 95-ppm resonances, to F_2 with J(Pt-F_2) = 160 Hz. Again, note the larger coupling of F_1 to Pt.

These results argue convincingly that these hydrogen-fluorine couplings occur by a through-space mechanism. An X-ray crystal structure of **11** is in progress.

The observed hydrogen-fluorine coupling to the axial pyrazolyl ring proton with the largest ^{195}Pt coupling constant confirms our initial assignment of this proton as the one at the 3 position.

(d) Five-Coordinate Allene Complexes of Platinum(II). In view of the unusual stability of the five-coordinate olefin- and acetyleneplatinum(II) poly(pyrazolyl)borate complexes, we decided to examine the reactions of Pt(CH$_3$)[HB(pz)$_3$] with a variety of allenes.

Pt(CH$_3$)[HB(pz)$_3$] reacted in about 4 hr with tetramethylallene to give a white crystalline complex. The ^{1}H nmr spectrum in the region δ 6-8 was consistent with a trigonal-bipyramidal structure in which the two equatorial pyrazolyl rings were inequivalent. We therefore assign structure **14** to this complex. An X-ray structure analysis of the platinum(0) complex[14] Pt[P(C$_6$H$_5$)$_3$]$_2$(CH$_2$=C=CH$_2$) showed that the coordinated end of the allene was in the PtP$_2$ plane and the uncoordinated double bond was bent backward by an angle of 38°. We have thus not drawn the C=C=C unit as a linear moiety. The nmr spectrum (Figure 5) of **14** showed the expected five peaks above δ 2.5 which could be assigned to the four allene methyl and one platinum methyl resonances. The two low-field resonances (Figure 5A and B) at δ 2.03 and 1.82 with Pt-H coupling constants of 2.5 and 8.5 Hz, respectively, are assigned to the two methyl groups on the uncoordinated end of the allene. The methyl resonances of Figure 5C and D at δ 1.26 and 1.07 with coupling constants to ^{195}Pt of 52.5 and 70.0 Hz, respectively, are assigned to the methyl resonances of the coordinated end of the allene. The high-field resonance, Figure 5E, is assigned to the platinum methyl group. The high-temperature nmr spectra of **14** (30-120°) were examined and the allene was stereochemically rigid to 110° at which temperature decomposition occurred.



14

Pt(CH$_3$)[HB(pz)$_3$] reacted very quickly with 1,1-dimethylallene ((CH$_3$)$_2$C=C=CH$_2$) to give a white crystalline complex. There were two possibilities for coordination of the allene: through either the CH$_2$=C or the (CH$_3$)$_2$C=C end of the molecule. The nmr spectrum showed the presence of only one isomer as evidenced by the observation of two allene methyl resonances at δ 2.08 and 1.78 with Pt-H coupling constants of 1.0 and 11.5 Hz, respectively. By comparing both the chemical shifts and ^{195}Pt coupling constants of these two resonances with the four methyl resonances of **14**, it is quite clear that 1,1-dimethylallene is coordinated through the C=CH$_2$ end of the molecule.

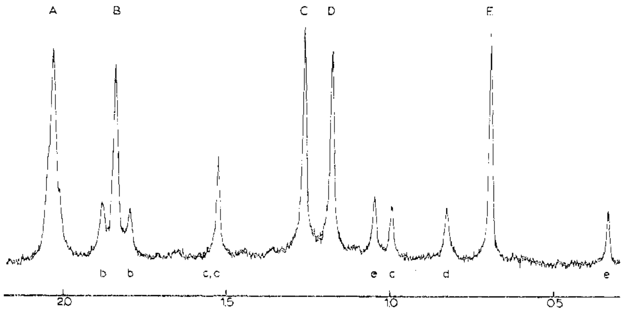


Figure 5. ^{1}H nmr spectrum of Pt(CH$_3$)[HB(pz)$_3$][(CH$_3$)$_2$C=C=C-(CH$_3$)$_2$] showing the presence of the four allene methyl resonances (A-D) and the platinum methyl resonance (E).

Methylallene (CH$_3$CH=C=CH$_2$) reacted very readily with Pt(CH$_3$)[HB(pz)$_3$] to give a stable 1:1 adduct. A total of four isomers are possible with the ligand and the nmr spectrum showed the presence of at least two. However, due to the complexity of the spectrum it was not possible to determine their stereochemistry.

(e) Five-Coordinate Platinum(II) Carbonyl Complexes. Pt(CH$_3$)[HB(pz)$_3$] readily reacts with carbon monoxide in dichloromethane to give a crystalline 1:1 adduct. In contrast to the nmr spectra of the acetylene, allene, and olefin complexes, the pyrazolyl proton resonances of Pt(CH$_3$)-[HB(pz)$_3$](CO) are very simple. Only three resonances are observed at δ 7.67, 7.57, and 6.25 in the ratio of 1:1:1. The high-field resonance appears as a triplet (^3J(H-H) = 2.0 Hz) with platinum satellites (^4J(Pt-H) = 5.0 Hz) and is assigned to the three 4-H protons. By means of a simple double-resonance experiment the low-field resonance is assigned to the three 3-H protons (^3J(Pt-H) = 9.0 Hz) and the peak at δ 7.57 is assigned to the three 5-H resonances. Since all three pyrazolyl rings are magnetically equivalent and ^{195}Pt coupling is observed to the 3-H and 4-H protons, we can conclude that (a) the hydrotris(1-pyrazolyl)borate ligand is stereochemically nonrigid and that (b) the molecule retains its five-coordinate structure (on the nmr time scale). On cooling the sample down to −120°, the nmr spectrum showed the presence of two 4-H resonances in the ratio of 2:1 as expected for a trigonal-bipyramidal structure.

We have described the preparation of Pt(CH$_3$)[B(pz)$_4$] and some of its acetylene derivatives.[4] The complexes are trigonal bipyramidal with the fourth pyrazolyl ring remaining uncoordinated. Carbon monoxide reacts very readily with this compound giving the complex Pt(CH$_3$)-[B(pz)$_4$](CO). The nmr spectrum in the region 6-8 ppm shows six resonances in the ratio 3:1:1:3:1:3. These resonances were easily assigned to the three equivalent coordinated pyrazolyl rings and the one uncoordinated ring. The fact that the uncoordinated ring does not contribute to the fluxional nature of the ligand may rule out a dissociation-association exchange. The most likely mode of fluxionality is therefore due to a propeller-like rotation of the three pyrazolyl rings about the C_{3v} axis of the ligand. This mode of fluxionality has been observed previously in other poly(pyrazolyl)borate complexes.[15]

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[14] M. Kadonaga, N. Yasuoka, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 1597 (1971).

[15] P. Meakin, S. Trofimenko, and J. P. Jenson, *J. Amer. Chem. Soc.*, 94, 5677 (1972).

(f) Bonding in the Acetylene, Allene, and Olefin Complexes. It is worth briefly commenting on the greater stability of these five-coordinate complexes compared with other trigonal-bipyramidal olefin and acetylene complexes of platinum(II). The carbon-carbon unsaturated bond of the organic molecule is constrained within the trigonal plane of the platinum and two trans donor atoms, L. The only filled platinum 5d orbital of appropriate symmetry for π back-bonding into the π^* orbital of the organic ligand is the $5d_{xy}$ orbital (z axis is perpendicular to the equatorial plane). Since the $[HB(pz)_3]^-$ ligand is anionic, some delocalization of negative charge onto the two equatorial nitrogen atoms trans to the organic moiety can be expected. The net effect is an enlargement of the Pt $5d_{xy}$ orbital with a concomitant increase in π back-bonding. This increased stability is not possible for the other five-coordinate olefin and acetylene complexes of platinum(II) where the trans ligands L are *neutral* atoms such as phosphorus or arsenic.

Conclusions

(1) The hydrotris(1-pyrazolyl)borate ligand has been shown to stabilize five-coordinate trigonal-bipyramidal olefin, allene, and carbonyl complexes of platinum(II).

(2) The pyrazolylborate ligands in the olefin and allene complexes are stereochemically rigid at room temperatures whereas for the carbonyl complexes they are fluxional.

(3) Where more than one geometrical isomer is possible for the olefin complexes, the ratio of isomers is dependent on the steric requirements of the olefin substituents.

(4) An unusual hydrogen-fluorine coupling has been observed between the platinum methyl protons or the axial 3-H proton and the fluorine atoms on fluoroolefin complexes. This interaction has been attributed to a through-space interaction.

(5) The observed Pt-H and H-F coupling constant data permitted the complete assignment of all 3-H, 4-H, and 5-H resonances of the pyrazolyl rings.

Experimental Section

The following chemicals were obtained commercially and were used without further purification: maleic anhydride, dimethyl maleate, diethyl fumarate, *p*-benzoquinone, crotonaldehyde, methacrylonitrile, methyl acrylate, and acrylonitrile from Eastman Organic Chemicals, Rochester, N. Y.; tetramethylallene from Columbia Organic Chemicals, Columbia, S. C.; 1,1'-dimethylallene from Pfaltz and Bauer Inc., Flushing, N. Y.; trifluoromethacrylonitrile from Pierce Chemical Co.; 1,1'-difluoroethylene and trifluoroethylene from Peninsular ChemResearch Inc. Tetrafluoroethylene was prepared by the method of Locke, *et al.*;[16] however, due to the lack of complete experimental details, the preparation is described below. $Pt(CH_3)[HB(pz)_3]$ was prepared as previously described.[5]

All reactions and recrystallizations were performed using "Spectro" Grade solvents without purification.

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

Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer, the samples being prepared as Nujol mulls between KBr plates.

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

a. **Preparation of $CF_2{=}CF_2$.** A three-neck 150-ml round bottom flask was fitted with a pressure-equalizing dropping funnel, a nitrogen inlet, and a trap cooled to the temperature of liquid nitrogen. Dimethylformamide (30 ml) and zinc dust (4 g) were placed in the flask with a magnetic stirring bar. The flask was placed in an oil bath preheated to 90° and was magnetically stirred. After about 15 min 1,2-dibromotetrafluoroethane (5 g) was placed in the dropping funnel and a slow stream of nitrogen was passed through the system. Over a period of 20 min the 1,2-dibromotetrafluoroethane was added to the dimethylformamide solution. Tetrafluoroethylene rapidly distilled from the flask and condensed in the liquid nitrogen trap. After the reaction was complete, the trap was connected to a vacuum line and its contents redistilled into a second liquid nitrogen trap. The yield was about 2 g.

b. **Preparation of $Pt(CH_3)[HB(pz)_3](CF_2{=}CF_2)$.** $Pt(CH_3)[HB(pz)_3]$ (0.40 g, 0.945 mmol) was placed in the bottom of a 20-ml thick-walled Carius tube and 5 ml of dichloromethane was added. Tetrafluoroethylene (3.0 mmol) was condensed into the tube, and the tube was sealed and shaken for 24 hr. The platinum polymer dissolved within a few hours to give a dark solution. The tube was then opened and the contents were washed into a 25-ml flask with dichloromethane. The solvent volume was reduced to about 3 ml and the solution was then passed through a short Florisil column, eluting with dichloromethane. A clear, colorless solution resulted. The volume was reduced to about 2 ml and pentane was added. After the solution had been cooled at $-14°$ for several hours, white crystals deposited. The crystals were filtered off and air-dried. The yield was 78%.

c. **Preparation of $Pt(CH_3)[HB(pz)_3](CH{=}CHCOOCO)$.** A suspension of $Pt(CH_3)[HB(pz)_3]$ (0.300 g, 0.710 mmol) and maleic anhydride (0.070 g, 0.710 mmol) in dichloromethane was magnetically stirred for 15 min to give a clear solution. The solution was passed through a 1-in. Florisil column, eluting with dichloromethane. The solvent volume was reduced and pentane was added to give white crystals. The yield was 84%.

d. **Preparation of $Pt(CH_3)[HB(pz)_3](CH_2{=}CHCN)$.** Acrylonitrile (0.100 ml) and $PtMe[HB(pz)_3]$ (0.280 g, 0.662 mmol) were suspended in 5 ml of dichloromethane and magnetically stirred for 20 min. The solution was chromatographed with dichloromethane to give a clear colorless solution. The solvent was removed to give an oil which was taken up in 2 ml of diethyl ether. A serum cap was fitted to the top of the flask which was then cooled to $-78°$ in Dry Ice for 30 min. Pentane was added dropwise from a 1-ml syringe to give a white precipitate. After an excess of pentane had been added, the flask was kept at $-78°$ for 1 hr. The serum cap was then removed, the solvents were decanted, and the white precipitate was dried under high vacuum. The yield was 65%.

e. **Preparation of $Pt(CH_3)[HB(pz)_3][(CH_3)_2C{=}C{=}C(CH_3)_2]$.** To a suspension of $Pt(CH_3)[HB(pz)_3]$ (0.310 g, 0.733 mmol) in 10 ml of dichloromethane was added tetramethylallene (0.20 ml). The solution was stirred for 4 hr and then passed through a 1-in. Florisil column, eluting with dichloromethane. The solvent was removed and the oil was dissolved in 1 ml of diethyl ether. Pentane (5 ml) was added and the solvents were allowed to evaporate slowly in the air to give white crystals. The yield was 58%.

f. **Preparation of $Pt(CH_3)[HB(pz)_3][(CH_3)_2C{=}C{=}CH_2]$.** A solution of $Pt(CH_3)[HB(pz)_3]$ (0.300 g, 0.710 mmol) and 1,1'-dimethylallene (0.100 ml) in 5 ml of dichloromethane was stirred for 15 min to give a clear solution which was passed through a 1-in. Florisil column. The solvent volume was reduced to about 1 ml and pentane was added. The flask was cooled for 12 hr to give white crystals. The solvents were decanted and the complex was dried under vacuum. The yield was 83%.

g. **Preparation of $Pt(CH_3)[HB(pz)_3](CO)$.** Carbon monoxide was bubbled through a suspension of $Pt(CH_3)[HB(pz)_3]$ (0.262 g, 0.595 mmol) in 10 ml of dichloromethane for 30 min. The solvent volume was reduced and the solution was passed through a short Florisil column, eluting with dichloromethane to give a clear colorless solution. The solvent was removed and the oil was taken up in 1 ml of diethyl ether. Pentane was slowly added to give white crystals. The flask was cooled for 12 hr and the complex was dried under vacuum. The yield was 78%; mp 92–94°. Infrared: $\nu(CO)$ 2088 cm^{-1}. Nmr ($CDCl_3$): $\delta(Pt\text{-}CH_3)$ 1.02, $^2J(Pt\text{-}H) = 70.0$ Hz; δ(4-H) 6.25, $^3J(H\text{-}H) = 2.0$ Hz, $^4J(Pt\text{-}H) = 5.0$ Hz; δ(3-H) 7.67, $^3J(Pt\text{-}H) = 9.0$ Hz; δ(5-H) 7.57. *Anal.* Calcd for $C_{11}H_{13}BN_6OPt$: C, 29.28; H, 2.90; N, 18.63. Found: C, 29.46; H, 2.96; N, 18.76.

h. **Preparation of $Pt(CH_3)[B(pz)_4](CO)$.** Carbon monoxide was bubbled through a suspension of $Pt(CH_3)[B(pz)_4]$ (0.110 g, 0.225 mmol) in 10 ml of dichloromethane. After about 5 min the polymer had dissolved so the volume was reduced and the solution was passed through a short Florisil column, eluting with diethyl ether. The volume of ether was reduced and pentane was added to give white crystals. The yield was 76%; mp 145–146°. Infrared: $\nu(CO)$ 2095 cm^{-1}. Nmr ($CDCl_3$): $\delta(Pt\text{-}CH_3)$ 0.90, $^2J(Pt\text{-}H) = 71.7$ Hz. Nmr for coordinated pyrazolyl rings: δ(4-H) 6.30, ^3J-

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(H–H) = 2.0 Hz; δ(3-H) 7.75; δ(5-H) 6.99. Nmr for uncoordinated pyrazolyl ring: δ(4-H) 6.39, ^3J(H–H) = 2.0 Hz; δ(3-H) 7.63, δ(5-H) 7.45 (these two assignments may be reversed). *Anal.* Calcd for $C_{14}H_{15}BN_8OPt$: C, 32.53; H, 2.92. Found: C, 32.59; H, 2.96.

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Registry No. $Pt(CH_3)[HB(pz)_3](CF_2{=}CF_2)$, 51548-82-4; $Pt(CH_3)[HB(pz)_3](CF_2{=}CH_2)$, 51548-83-5; $Pt(CH_3)[HB(pz)_3](CH{=}CHCOOCO)$, 51607-50-2; $Pt(CH_3)[HB(pz)_3]$[*cis*-$(CH_3)O_2CCH{=}CHCO_2(CH_3)$], 51607-51-3; $Pt(CH_3)[HB(pz)_3]$[*trans*-$(C_2H_5)O_2CCH{=}CHCO_2(C_2H_5)$], 51607-52-4; $Pt(CH_3)[HB(pz)_3]$(*p*-OC_6H_4O), 51607-53-5; $Pt(CH_3)[HB(pz)_3][CH_2{=}C{=}C(CH_3)_2]$, 51607-54-6; $Pt(CH_3)[HB(pz)_3][(CH_3)_2C{=}C{=}C(CH_3)_2]$, 51607-55-7; $Pt(CH_3)[HB(pz)_3]$(*trans*-$CH_3CH{=}CHCHO$) (9), 51607-56-8; $Pt(CH_3)[HB(pz)_3]$(*trans*-$CH_3CH{=}CHCHO$) (**10**), 51607-57-9; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CH_3)CN]$ (7), 51607-58-0; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CH_3)CN]$ (8), 51607-59-1; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CF_3)CN]$ (**13a**), 51548-84-6; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CF_3)CN]$ (**13b**), 51607-60-4; $Pt(CH_3)[HB(pz)_3][CH_2{=}CHCO_2(CH_3)]$ (*cis*-Me, CO_2Me), 51607-61-5; $Pt(CH_3)[HB(pz)_3][CH_2{=}CHCO_2(CH_3)]$ (*cis*-Me, H), 51607-37-5; $Pt(CH_3)[HB(pz)_3][CH_2{=}CH(CN)]$ (*cis*-Me, H), 51540-56-8; $Pt(CH_3)[HB(pz)_3][CH_2{=}CH(CN)]$ (*cis*-Me, CN), 51607-38-6; $Pt(CH_3)[HB(pz)_3](CF_2{=}CFH)$ (**12a**), 51540-57-9; $Pt(CH_3)[HB(pz)_3](CF_2{=}CFH)$ (**12b**), 51607-39-7; $Pt(CH_3)[HB(pz)_3](CH_3CH{=}C{=}CH)$, 51567-33-0; $Pt(CH_3)[HB(pz)_3](CO)$, 51703-30-1; $Pt(CH_3)[B(pz)_4](CO)$, 51567-36-3; $Pt(CH_3)[HB(pz)_3]$, 39395-33-0; $Pt(CH_3)[B(pz)_4]$, 50921-19-2; ^{195}Pt, 14191-88-9.

Contribution from the Departments of Chemistry, Colorado State University,
Fort Collins, Colorado 80521, and University of California, Irvine, California 92664

Facile Dissociation of a Copper Porphyrin. Chlorocopper(II) *N*-Methyltetraphenylporphine

DAVID K. LAVALLEE* and ALLEN E. GEBALA

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All copper complexes of porphyrins studied to date are extremely stable toward dissociation. The complex chloro-*N*-methyltetraphenylporphinecopper(II), however, undergoes dissociation readily on dilution in solutions of dimethylformamide. At a concentration of 3.6×10^{-4} *M*, the copper ion is equally complexed and solvated. The preparation and characterization of *N*-methyltetraphenylporphine is described. The acid dissociation constants of this porphyrin in nitrobenzene are $pK_3 = 5.64$ and $pK_4 = 3.85$ compared to values for tetraphenylporphine of $pK_3 = 4.38$ and $pK_4 = 3.85$. The nature of the complexes in terms of true complex or ion-pair behavior is investigated by conductivity measurements in DMF, by elemental analysis of isolated solids, and by the method of Job's plots. The species are evidently complexes rather than ion pairs, despite the similarity of their visible absorption spectra to monoprotonated *N*-methyltetraphenylporphine.

Introduction

N-Methylporphyrins[1-3] and some metal complexes formed with them[2] have been known for several years. However, little work has been done regarding the nature of bonding of these complexes, their stability constants, and formation kinetics and mechanism. Recently interest has revived in the synthesis of *N*-alkylporphyrins[4,5] and in the metal complexes formed with them.[6,7] Zinc- and copper–chloro complexes of *N*-methylporphyrins were prepared, a zinc ion assisted demethylation of an *N*-methylporphyrin has been observed,[6] and the kinetics of the acid-catalyzed solvolysis of a zinc *N*-methylporphyrin has been described.[7] A comparison has also been made of the incorporation of zinc and cadmium into etioporphyrin III and *N*-methyletioporphyrin III.[8]

The study of metal complexes of *N*-methylporphyrins seems especially important in light of Hambright's recently proposed mechanism for metal ion incorporation into porphyrin molecules.[9] In this mechanism, one species (a metal ion, proton, or *N*-alkyl group) deforms the porphyrin, allowing rapid metal incorporation from the opposite side of the porphyrin. The mono-*N*-methylporphyrin, therefore, may serve as a model for the distorted porphyrin which incorporates the metal ion. (See Figure 1.)

In this study, the mono-*N*-methyl derivative of the widely studied porphyrins α,β,γ,δ-*meso*-tetraphenylporphine has been synthesized and characterized. The copper–chloro and cobalt–chloro complexes have been studied to determine whether they are best described as true complexes or as ion pairs—a feature of metalloporphyrin chemistry which has evoked considerable debate.[10-13] The facile equilibrium of solvated and complexed copper in DMF is described.

Experimental Section

All reagents were at least of reagent grade quality. Perchloric acid was G. F. Smith double-distilled. Dimethylformamide (DMF) was distilled under reduced pressure from benzene, shaken with BaO

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* To whom correspondence should be addressed at Colorado State University.

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