dimer. Considering one NCS^- bridge, the unpaired electrons on one nickel will bond to the nitrogen end of the thiocyanate with the σ orbitals of the bridge, while the unpaired electrons on the second nickel will bond through the π orbitals of the bridge. Thus the unpaired electrons from the two metal centers are delocalized into orthogonal bridge orbitals on each NCS^- bridge and a ferromagnetic effect is observed for this dimer.

Antiferromagnetic exchange of the oxalate-bridged Ni(II) dimer is also explicable on simple symmetry considerations. The oxalate bridge is *symmetric* in its interaction with the two nickel ions. If the unpaired electrons on one nickel ion are delocalized into a certain bridge molecular orbital, because of the symmetry of this bridge the unpaired electrons on the second nickel will also be delocalized into the same bridge molecular orbital. Thus, in the case of the oxalate-bridged nickel(II) dimer, there are only antiferromagnetic mechanisms operative. The e_g (O_h designation) orbitals on the nickel ions span the a_{1g} and b_{1g} representations in the D_{2h} point group. CNDO/2 calculations were completed on the oxalate dianion and it was found that in the ten highest energy filled orbitals there are two a_{1g} and two b_{1g} symmetry orbitals. Bonding propagated through these four bridge orbitals leads to the observed antiferromagnetic interaction.

The squarate-bridged system would, on the basis of the above discussion, be expected to display some antiferromagnetic coupling. The fact that the observed J ($\simeq -0.4$ cm^{-1}) is small can be qualitatively rationalized. In D_{4h} symmetry (appropriate for the squarate-bridged nickel dimer moiety), the unpaired d electrons would be in a_{1g} and b_{1g} symmetry orbitals. Comparison of CNDO/2 calculations on the oxalate and squarate dianions shows that in the case of squarate the appropriate symmetry bridge orbitals lie at lower energy than those in the oxalate dianion. Even further, the squarate dianion is larger than the oxalate dianion and this would result in smaller expectation values of e^2/r_{ij} for the various molecular orbitals.

Conclusion

Antiferromagnetic exchange has been detected in oxalate- and squarate-bridged nickel(II) dimers. It is shown that the symmetry of the bridge is crucial in determining the sign and magnitude of the exchange interaction between bridged metal atoms.

Registry No. $[Ni_2(trien)_2(C_2O_4)](ClO_4)_2$, 38560-48-4; $[Ni_2(macro)_2(C_2O_4)](ClO_4)_2$, 38547-88-5; $[Ni_2(macro)_2(C_4O_4)](ClO_4)_2$, 38585-02-3.

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Contribution from the Department of Chemistry, The University of Western Ontario, London, Canada

Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. V. A Comparative Study with π-Olefinic Complexes

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Cationic methylplatinum complexes *trans*-$[PtCH_3(un)\{P(CH_3)_2C_6H_5\}_2]PF_6$, where un = an olefin, diene, allene, vinyl ether, allyl alcohol, and allylamine, have been prepared from the reaction of *trans*-$[PtCH_3(acetone)\{P(CH_3)_2C_6H_5\}_2]PF_6$ with the appropriate unsaturated hydrocarbon un. With cyclopentadiene, $[(h^5\text{-}C_5H_5)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ and methane were formed, while for un = diallyl ether and allylacetamide a disproportionation reaction occurred leading to $[PtCH_3\{P(CH_3)_2C_6H_5\}_3]PF_6$ and $[PtCH_3(un)P(CH_3)_2C_6H_5]PF_6$ in which un acts as a chelating ligand. π-Allene complexes were only stable below 0°; above this temperature insertion into the methylplatinum bond occurred with the formation of cationic π-allylic complexes. The nature of the platinum–olefin bond is discussed on the basis of vibrational and variable-temperature nmr spectra. The bonding, trans influences, and reactivities of these π-olefinic cations are compared to those observed in closely related (i) acetylenic complexes *trans*-$[PtCH_3(RC\equiv CR')\{P(CH_3)_2C_6H_5\}_2]PF_6$ and (ii) cationic hydride olefinic complexes *trans*-$[PtH(un)(PR_3)_2]PF_6$.

Introduction

Metal-olefin and -acetylene complexes both utilize a synergic bonding mechanism:[1,2] acetylene or olefin π to metal dsp and metal d to olefin or acetylene π^*. Therefore it is not surprising that analogous series of metal complexes are known, *e.g.*, $\{P(C_6H_5)_3\}_2Pt(un)$ and $[PtCl_3(un)]^-$ where un = an acetylene[3-9] or an olefin.[9-12] However, the formation of a stable metal-olefin complex does not necessarily imply the equally facile formation of a stable acetylene complex, and *vice versa*. While platinum complexes of the form $[PtCl_3(un)]^-$ and $PtCl_2(un)L$, where L = pyridine or ammonia, are readily formed with simple olefins,[12,13] only acetylenes $RC\equiv CR'$, with bulky or functional groups R and R$'$, which can interact with the metal or one of the other

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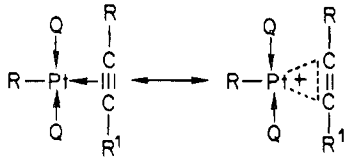
ligands, give stable complexes.[5,6,9] Differences between metal-olefin and metal-acetylene bonding arise from (i) differences in the relative energies of the olefin and acetylene π orbitals and (ii) the presence of two acetylenic π orbitals compared to one olefinic. It has been suggested that acetylenes should be better σ donors and better π acceptors than olefins since their π orbitals are lower in energy. Similarly, when both π orbitals can be involved in the bonding (as in zerovalent platinum complexes), acetylenes should have stronger metal-ligand interaction. However, when only one π orbital and its π* counterpart may participate (as in platinum(II) complexes), the synergic mechanism destabilizes the other π orbital causing the complex to act as a Lewis base, thus favoring polymerization over the formation of a stable complex unless the former is chemically or sterically opposed.[14]

We have previously described[15,16] the preparation and physical properties of cationic acetylenic complexes *trans*-$[PtCH_3(RC{\equiv}CR')Q_2]PF_6$, I, where $Q = P(CH_3)_2C_6H_5$ and R and R′ are alkyl or aryl groups. In contrast to other platinum(II)-acetylene complexes[5,6,9] the presence of bulky or functional groups R and R′ was not required to allow isolation of I. However, other acetylenes did show remarkable reactivity toward rearrangement and/or nucleophilic addition reactions leading to acetylide,[15] alkoxycarbene,[15,17,18] cyclobutadiene,[18,19] or vinyl ether[16] complexes depending on R and R′ and the solvent. We suggested[19,20] that these products are derived from reactions of platinum-induced carbonium ions I′ formed by delocalization of the positive charge over the acetylene moiety.



I I′

We have now prepared cationic olefinic complexes *trans*-$[PtCH_3(un)Q_2]PF_6$, II, where un = an olefinic ligand, in order to compare (i) the bonding and (ii) the reactivity of these coordinated π-bonding ligands with those of acetylenic complexes I.

Results and Discussion

Formation and Isolation of π Complexes. The general method for the preparation of the π complexes reported here is shown below in eq 1, where $Q = P(CH_3)_2C_6H_5$

$$\textit{trans-}[PtCH_3(acetone)Q_2]PF_6 + \text{un} \underset{}{\overset{CH_2Cl_2}{\rightleftharpoons}} \underset{\text{II}}{\textit{trans-}[PtCH_3(un)Q_2]PF_6} + \text{acetone} \quad (1)$$

and un = an unsaturated ligand. The dependence of this type of displacement reaction on the choice of solvent has been previously discussed.[21] We thus obtained II, un = $CH_2{=}CH_2$, $CH_2{=}CHCH_3$, $CH_2{=}CHOCH_3$, $CH_2{=}CHOC_2H_5$, $CH_2{=}CHCH_2OH$, $CH_2{=}CHCH_2NH_2$, $CH_2{=}C{=}CH_2$ and $CH_2{=}CHCH{=}CH_2$, as white or pale yellow crystalline solids. However, similar reactions involving un = *cis*- and *trans*-but-2-ene and stilbene were unsuccessful. Molecular models suggest that steric factors play an important role in the formation and isolation of II, un = RCH=CHR′. Due to its planar geometry, coordination of an olefin RCH=CHR′ to the $[CHPtQ_2]^+$ unit causes severe steric repulsion with the dimethylphenylphosphine ligands; this contrasts with acetylenic complexes I in which the acetylenic substituents are collinear with the acetylenic triple bond. Attempts to prepare II where $Q = As(CH_3)_3$ were unsuccessful and lead to formation of $[PtCH_3Q_3]^+$ salts together with other decomposition products. This situation closely parallels that previously observed[16] in the preparation of I, $Q = As(CH_3)_3$.

The complexes II were soluble in, and only slowly decomposed by, chlorinated solvents such as dichloromethane and chloroform. In polar oxygen-containing solvents, extensive dissociation occurred according to eq 2 where

$$\text{II} + \text{solvent} \rightleftharpoons \textit{trans-}[PtCH_3(solvent)Q_2]PF_6 + \text{un} \quad (2)$$

solvent = acetone or methanol. Again, this parallels the lability of the coordinated acetylene in I.[16,21]

II, un = $CH_2{=}C{=}CH_2$, was only stable in solution below 0°. Above this temperature insertion into the methylplatinum bond occurred with the formation of *cis*-$[Pt(h^3\text{-}C_4H_7)Q_2]PF_6$ where C_4H_7 is 2-methallyl. Similarly, reactions involving tetramethylallene, $(CH_3)_2C{=}C{=}C(CH_3)_2$, gave the pentamethallyl complex *cis*-$[Pt(h^3\text{-}C_8H_{15})Q_2]PF_6$ above 0°, although we were unable to isolate the π-tetramethylallene complex II as a crystalline product. Analogous reactions occurred for $Q = As(CH_3)_3$ and thus support the formation of the reactive and transient species II, $Q = As(CH_3)_3$ and un = allene.

For un = cyclopentadiene, reaction 1 gave the cyclopentadienyl cationic complex $[Pt(h^5\text{-}C_5H_5)Q_2]PF_6$. The elimination of the platinum methyl group as methane which occurs in this reaction may be compared to acetylide formation[15,19] in the reactions of terminal acetylenes (notably phenylacetylene) with $[CH_3PtQ_2]^+$.

Reaction 1 involving un = diallyl ether or allylacetamide led to formation of $[PtCH_3Q_3]^+$ and $[PtCH_3(un)Q_3]^+$ salts.

Analytical and other characterization data for the π complexes are given in Table I.

Vibrational Spectra. All the organoplatinum complexes showed the characteristic bands of PF_6^- and $P(CH_3)_2C_6H_5$ or $As(CH_3)_3$.[22] Assignments of ν_{str}(Pt-C) for the methylplatinum group in II are given in Table I and suggest, by a comparison[16] with I, that the olefinic double bond and the acetylenic triple bond exert similar trans influences.

Values of ν_{str}(C=C) quoted in Table I should be considered as characterization data. Coupling to other vibrations of the olefin, strain within the olefin, and the proximity of polar groups to the carbon-carbon double bond preclude any definite assignment.[9] However, by a comparison with previous assignments[23,24] of ν_{str}(C=C) in $K[PtCl_3(un)]$ and $PtCl_2(un)L$, where L = a substituted pyridine and un = C_2H_4 and $CH_3CH{=}CH_2$, the complexes II, un = C_2H_4 and $CH_3CH{=}CH_2$, show a smaller reduction from that of the free olefin

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Table I. Analytical and Characterization Data for Some Cationic Organoplatinum(II) π Complexes

		Analysis, %									Vibrational spectra,[c] cm^{-1}		
		C		H		N		Solubilities[b]					
Compd ($Q = P(CH_3)_2C_6H_5$; $A = As(CH_3)_3$)	Dec pt,[a] °C	Calcd	Found	Calcd	Found	Calcd	Found	CH_2Cl_2	$CHCl_3$	$(CH_3)_2CO$	Pt-CH_3 ν_{str}(Pt–C)	ν_{str}-(C═C)	Other
trans-[$PtCH_3(CH_2{=}CH_2)Q_2$]PF_6	135–140	34.60	34.66	4.44	4.14			vs	s	diss	549	1551	
trans-[$PtCH_3(CH_3CH{=}CH_2)Q_2$]PF_6	95	35.66	35.42	4.63	4.52			vs	s	diss	542	1551	
trans-[$PtCH_3(CH_2{=}C{=}CH_2)Q_2$]$PF_6$	95	35.77	35.50	4.36	4.65			vs	s	diss	545	1850[d]	
cis-[$Pt(\pi\text{-}C_4H_7)Q_2$]PF_6	150–152	35.77	35.68	4.36	4.56			vs	s	vs			453, 382, 353[e]
cis-[$Pt(\pi\text{-}C_8H_{15})Q_2$]$PF_6$	173–178	39.61	39.32	5.13	4.88			vs	vs	vs			
cis-[$Pt(\pi\text{-}C_4H_7)A_2$]PF_6	230–235	18.90	19.27	3.97	3.60			vs	vs	vs			460, 382, 353[e]
[$PtCH_3(CH_3CONHCH_2CH{=}CH_2)Q$]$PF_6$	145	28.38	29.02	3.92	3.92	2.36	2.02	ss	ss	ss	555	1545	ν_{str}(C═O) 1610, ν_{str}(N–H) 3410[d]
trans-$PtCH_3(CH_2{=}CHCH{=}CH_2)Q_2$]$PF_6$	90	36.79	36.47	4.56	4.28			I	I	diss	550	MO	
trans-$PtCH_3(CH_2{=}CHOCH_3)Q_2$]$PF_6$	118–120	34.83	34.85	4.53	.57			vs	s	diss	545	1570	
trans-$PtCH_3(CH_2{=}CHOC_2H_5)Q_2$]$PF_6$	115–120	35.85	35.83	4.73	4.58			vs	vs	diss	548	1545	
trans-$PtCH_3(CH_2{=}CHCH_2OH)Q_2$]$PF_6$	130	34.73	34.71	4.52	4.36			vs	vs	diss	dec	1545	
trans-$PtCH_3(CH_2{=}CHCH_2NH_2)Q_2$]$PF_6$	123–126	34.88	34.96	4.69	4.57			vs	s	vs	552	1640	
[$Pt(\pi\text{-}C_5H_5)Q_2$]PF_6	185–187	37.00	37.10	4.00	3.74			s	ss	vs			
$PtMe(OHCNMe_2)Q_2$]PF_6	123–125	35.58	35.40	4.64	4.37	2.02	2.00	vs	s	diss	576		

[a] Except for the π-allyl compounds for which melting points are given. [b] Abbreviations: vs, very soluble, 100 mg ml^{-1}; s, soluble, >50 mg ml^{-1}; ss, slightly soluble, >5 mg ml^{-1}; I, insoluble, <mg ml^{-1}; diss, dissociates according to eq 2 (see text). All compounds are insoluble in nonpolar organic solvents. [c] Unless noted otherwise, Raman values ±2 cm^{-1}. [d] Infrared values ±3 cm^{-1}. [e] Pt–allyl stretching vibrations; see ref 33–35.

Table II. ^1H Nmr Data[a] for the Complexes *trans*-[$PtCH_3(un)L_2$]PF_6 and Pt(un′)[L_2]PF_6

			Platinum methyl			L methyls				Vinylic protons			
L[b]	un, un′	Solvent	$\delta(CH_3)$	^2J(Pt–H)	^3J(P–H)	$\delta(CH_3)$	^3J(Pt–H)	$^2J + {}^4J$(P–H)	T,[c] °C	δ	J(Pt–H)	J(P–H)	Other
Q	$CH_2{=}CH_2$	$CHCl_3$	−0.83	74.2	7.2	−1.81	29.5	7.0	−50(?)	−4.12	36.8	2.7	
Q	$CH_3CH{=}CH_2$	CD_2Cl_2	−0.77	73.5	7.7	−1.83	30.0	7.0	10	−4.00[e]	~37.5	. . .	
Q	$CH_2{=}C{=}CH_2$	CD_2Cl_2	−0.87	72.0	7.5	−1.81	30.0	7.5	−30	−3.71[e]	37.0	~3.0	Free $\delta(=CH_2)$ −5.22
Q	$CH_2{=}CHCH{=}CH_2$	$CHCl_3$	−0.82	75.0	7.5	−1.80	30.0	7.2	. . .	−4.00[e]	. . .	. . .	
Q	$CH_3OCH{=}CH_2$	CD_2Cl_2	−0.64	72.0	7.2	−1.82	29.2	7.0	−55	−3.38[e]			$\delta(OCH_3)$ −3.61
Q	$C_2H_5OCH{=}CH_2$	CD_2Cl_2	−0.65	72.7	7.5	−1.80	29.5	7.0	−55	−3.29[e]			$\delta(OCH_2-)$ 3.93, $\delta(-CH)$ −1.30
Q	$CH_2{=}CHCH_2NHCOCH_3$[d]	$CHCl_3$	−1.01	64.0	2.5	−1.64	46.0	6.8		−4.50 to −3.60[e]	Unresolved couplings		$\delta(CHC(O)-)$ −2.23
Q	$H_2NCH_2CH{=}CH_2$	$CHCl_3$	−1.12	74.0	7.6	−2.29	32.2	6.8		−4.75[e]	0	0	$\delta(-CH_2M)$ −2.95
						2.39	33.5	6.6					
Q	h^3-C_4H_7	$CHCl_3$				−1.50	37.5	J(P–H) = 10.5		A −2.85[f]	42.7	9.0	$\delta(CH_3(C))$[f] −1.61, J(Pt–H) = 57.7, J(R–H) ≈ 0
						−1.48	36.5	J(P–H) = 10.5		B −3.64	<0.5	<0.5	
A	h^3-C_4H_7	$CHCl_3$				−1.70	23.5			A −2.60	49.0		$\delta(CH_3(C)$ −1.88, J(Pt–H) = 65.0
										B −4.03	~7.0		
Q	h^5-C_5H_5	CD_2Cl_2				−1.95	40.0	11.5					$\delta(C_5H_5)$ −6.37, J(Pt–H) = 11.2, J(P–H) = 1.2
Q	$OCHN(CH_3)_2$	$CHCl_3$	−0.49	88.0	7.1	−1.66	32.8	7.8					$\delta(=M^{CH^1}_{CH^2})$ $\delta(CH_3{}^1)$ −2.65, $\delta(CH_3{}^2)$ 3.07

[a] Chemical shifts (δ) in ppm from internal reference TMS; coupling constants J in Hz. All data recorded at 30°, 100 MHz. [b] Ligands: $Q = P(CH_3)_2C_6H_5$, $A = As(CH_3)_3$. [c] T = coalesence temperature; see Figure 2 and text. [d] Data for [$PtCH(CH{=}CHCHMNCOCH)Q$]$^+$ give a speculative assignment; see text. [e] Center of complex resonance; see text. [f] Stereochemistry of A, B, C is shown in the caption to Figure 3.

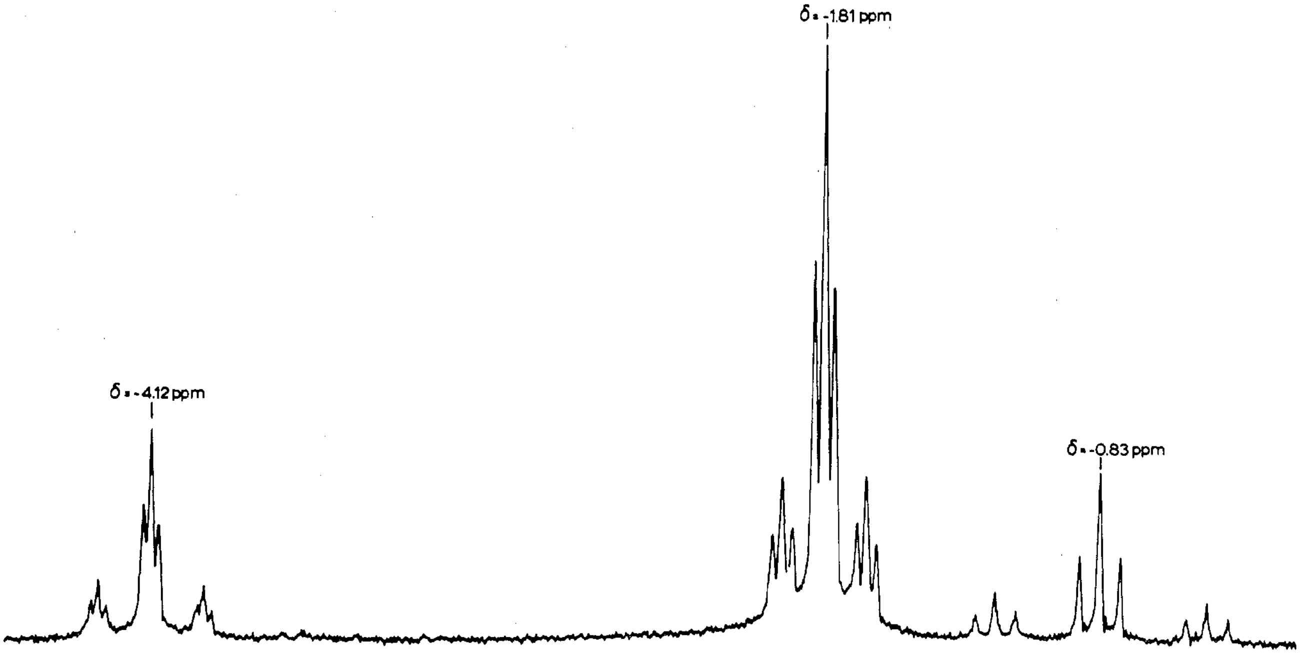

Figure 1. ^1H nmr spectrum of *trans*-$[PtCH_3(CH_2{=}CH_2)\{P(CH_3)_2C_6H_5\}_2]PF_6$ recorded in $CHCl_3$ solution at 30°, 100 MHz. Phenyl proton resonances are not shown.

value. This may be taken to indicate a weaker platinum-olefin bond in II, a conclusion which is to be expected in view of the sensitivity of "metal back-bonding" to the electron density on the metal. Several workers have noted that the stability of platinum(II)-olefin complexes decreases as the overall charge on the complex becomes more positive.[9] Similarly, a comparison of $\nu_{str}(C{=}C)$ for the cumulative double bond in II, un = $CH_2{=}C{=}CH_2$ (see Table I), with previous assignments for allene complexes of Rh(I)[25] and Pt(0)[26] is consistent with the expected order of metal d to allene π^* interaction, *viz.*, $Pt(0) \sim Rh(I) > Pt(II)$.

Recent spectroscopic studies[27] of Zeise's salt, $K[PtCl_3(C_2H_4)]$, and its hydrate favor assignment of $\nu_{str}(C{=}C)$ to a strong polarizable Raman band at 1243 cm^{-1}. We observe a strong polarizable bond in the Raman spectrum of II, un = C_2H_4, at 1275 cm^{-1}. The confusion over the assignment $\nu_{str}(C{=}C)$ in these ethylene complexes is due to strong coupling of $\nu_{str}(C{=}C)$ with $\delta(CH_2)$ (in-plane, "scissors," deformation).[28] The controversial assignment of $\nu_{str}(C{=}C)$ in Zeise's salt had led to differing views on the nature of the platinum-olefin interaction: a weakly perturbed double bond[2,9,23,24,29] *vs.* a metallocyclopropane structure.[27,30,31] We believe an analogy to a cyclopropane derivative[31] is inapplicable for II. This point is clearly evident from our recent ^{13}C nmr studies.[32]

Raman bands at 432, 423, and 373 cm^{-1} for II, un = C_2H_4, and at 404 and 382 cm^{-1} for II, un = $CH_3CH{=}CH_2$, are attributable to the platinum-olefin moiety. We expect a platinum-olefin stretching mode in this region by a comparison with previous assignments,[23,24,27,31] but the extent of our studies precludes any definite assignment.

II, un = $CH_2{=}CHCH_2OH$, shows $\nu_{str}(O{-}H)$ *ca.* 3550 cm^{-1} and thus offers no evidence for coordination *via* oxygen. On the other hand II, un = $CH_2{=}CHCH_2NH_2$, shows $\nu_{str}(C{=}C)$ 1645 cm^{-1} indicating coordination *via* nitrogen with little or no platinum-olefin interaction.

Assignment of the platinum-allyl stretching vibration in *cis*-$[Pt(h^3\text{-}C_4H_7)Q_2]PR_6$ (see Table I) is made by comparison with previous studies.[33-35]

^1H Nmr Studies and Structural and Bonding Considerations. ^1H nmr spectra were obtained from dichloromethane-d_2 or chloroform solutions over a temperature range +60 to −80°. Relevant nmr parameters are presented in Table II.

***trans*-$[PtCH_3(un)\{P(CH_3)_2C_6H_5\}_2]PF_6$, II.** The phosphine methyl proton resonances in II appeared as 1:2:1 triplets due to the virtual coupling of the mutually trans ^{31}P nuclei.[36] Further coupling to ^{195}Pt ($I = 1/2$, 34% natural abundance) gives satellites of one-fourth intensity. A similar pattern was observed for the platinum methyl protons due to coupling to two equivalent ^{31}P nuclei and to ^{195}Pt. The vinylic protons of the coordinated olefinic ligand un occurred *ca.* −4.00 ppm from TMS (upfield from the free olefin) and show coupling to both ^{195}Pt and ^{31}P. For un = C_2H_4 this leads once again to a triplet of triplets (shown in Figure 1) but for monosubstituted alkenes $RCH{=}CH_2$ further proton-proton coupling occurs and the resultant spectra were complex and ill resolved.

We have previously suggested[16,21,37] that $^2J(Pt{-}H)$ for the

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(34) D. M. Adams and A. Squire, *J. Chem. Soc. A*, 1808 (1970).

(35) G. Davidson and D. C. Andrews, *J. Chem. Soc., Dalton Trans.*, 126 (1972).

(36) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

methylplatinum protons and ^3J(Pt-H) for the phosphine methyl protons may be used to evaluate the trans-influence and π-acceptor properties of neutral ligands, L, in cations of the type *trans*-$[PtCH_3(L)\{P(CH_3)_2C_6H_5\}_2]^+$. ^2J(Pt-H) for the methylplatinum protons in II falls within the range 72.0-75.0 Hz, which suggests that the olefinic double bond is comparable in trans influence to an sp^2 or sp^3 nitrogen donor,[21] *e.g.*, pyridine or ammonia. ^2J(Pt-H) for II, un = $CH_2{=}C{=}CH_2$, $CH_2{=}CH_2$, $CH_2{=}CHCH{=}CH_2$, and $CH_3C{\equiv}CCH_3$,[17,21] increases down the series $CH_2{=}C{=}CH_2$ to $CH_3C{\equiv}CCH_3$ which suggests that the trans influence (*i.e.*, the nmr trans influence[38]) correlates, at least approximately, with the polarizability of the π bond.[39] The π-acceptor properties of these olefinic ligands is indicated[17] by the relatively small magnitude of ^3J(Pt-H) for the phosphine methyl protons: $^3J(\text{Pt-H}) \approx 29$ Hz for II except for II, un = $CH_2{=}CHCH_2NH_2$, which is N bonded and shows $^3J(\text{Pt-H}) \approx 33$ Hz (see Table II).

The platinum d to olefin π^* interaction is favored when the carbon-carbon double-bond axis is perpendicular to the $[CH_3PtQ_2]$ plane.[9,40] Variable-temperature ^{1}H nmr spectra of II, un = $RCH{=}CH_2$, show that rotation about the platinum-olefin bond is a function of temperature since the phosphine methyl proton resonances which appear as 1:2:1 triplets at room temperature (*e.g.*, shown in Figure 1) become two sets of overlapping triplets at lower temperatures (thus indicating the adoption of a preferred conformer in which the plane of symmetry about the CH_3PtP_2 unit is no longer present). This situation is shown in Figure 2 which shows the temperature dependence of the phosphine methyl proton resonances for II, un = $CH_3CH{=}CH_2$. It is interesting to note that when an asymmetric olefin $RCH{=}CH_2$ adopts a preferred conformation, either perpendicular to the CH_3PtP_2 plane (to maximize Pt d to olefin π^* interaction) or slightly distorted from this position (to minimize steric interaction with the $P(CH_3)_2C_6H_5$ ligands), there are four inequivalent phosphine methyl groups: a situation which should yield four sets of overlapping triplets in the ^{1}H nmr spectrum. The observed spectra consisting of two overlapping sets of triplets (as shown in Figure 2) must arise from accidental magnetic degeneracy.

Other workers[41-44] have observed the temperature dependence of olefin rotation in platinum(II)-olefin complexes. Ideally a comparison of the temperatures at which olefin rotation is frozen out would allow a comparison of the relative magnitudes of π bonding (Pt d to olefin π^*) in these complexes. However, steric factors normally invalidate such arguments;[43,44] indeed for II, steric factors are probably dominant: rotation is restricted below 10° for II, un = $CH_3CH{=}CH_2$, but for un = $CH_2{=}C{=}CH_2$, in which the methylene group is collinear with the coordinated double bond (see discussion below), rotation is only restricted below −30°. The ethylene 1:2:1 triplets (shown in Figure 1) become broad below −50°, possibly due to restricted platinum-ethylene rotation which transforms the simple A_2X_4 spectrum to the more complex $AA'X_4$ spectrum.

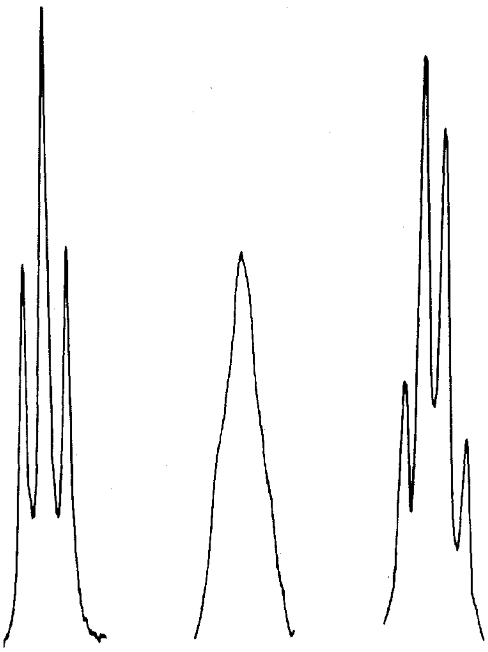
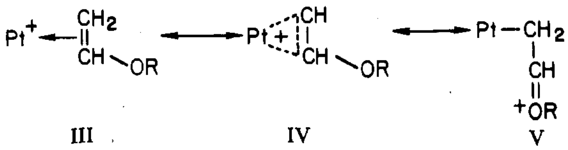


Figure 2. ^{1}H nmr spectrum of the phosphine methyl proton resonances in *trans*-$[PtCH_3(CH_3CH{=}CH_3)\{P(CH_3)_2C_6H_5\}_2]PF_6$ recorded in $CHCl_3$ solution, 100 MHz. Left to right at 25, 10, and 0°. platinum satellites are ommitted.

The π-vinyl ether complexes, II, un = $CH_2{=}CHOCH_3$ and $CH_2{=}CHOC_2H_5$, show free platinum-olefin rotation down to −55°. This is somewhat unexpected since the steric requirements of these π-vinylic ligands are comparable to that of $CH_3CH{=}CH_2$. The π-bonded vinyl ether ligands also differ from II, un = $CH_3CH{=}CH_2$, by showing (i) a greater nmr trans influence, (ii) a larger upfield shift of the vinylic protons, and (iii) a larger value of J(Pt-H) for these olefinic protons. A possible rationale for these differences is that the oxygen lone pairs may participate in the bonding and assist in delocalization of the positive charge. Pictorially this can be represented by the resonance structures III-V.



III IV V

For II, un = $CH_2{=}CHCH_3$, any contribution of type V would involve the less favorable hyperconjugation $Pt{-}CH_2{-}CH{=}CH_2,H^+$. A significant contribution from V also offers an explanation[45] for the inability of these π-vinyl ether complexes to rearrange to the thermodynamically more stable alkoxycarbene complexes *trans*-$[PtCH_3(C(OR)CH_3)Q_2]PF$ and, similarly, may account for the anomalous reactivity of vinyl ethers with hydridoplatinum cations of the type *trans*-$[PtH(un)Q_2]^+$.[46]

The ^{1}H nmr spectrum of II, un = $CH_2{=}C{=}CH_2$, shows a temperature-independent (0 to −60°) inequivalence of the

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[37] A linear correlation between $^1J(^{195}Pt-^{13}C)$ and $^2J(^{195}Pt-^1H)$ has been observed for those cations and supports this argument: M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).

[38] T. G. Appleton, H. C. Clark, and L. E. Manzer, submitted for publication in *Coord. Chem. Rev.*

[39] "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., June 1969.

[40] All X structures of platinum(II)-olefin, -acetylene, and -allene complexes have shown this is the preferred geometry.

[41] M. Orchin and P. J. Schmidt, *Coord. Chem. Rev.*, 3, 345 (1968).

[42] M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.*, 2, 123 (1968).

[43] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

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

[45] See also discussion in ref 19.

[46] H. Kurosawa and H. C. Clark, *Inorg. Chem.*, 12, 357 (1973).

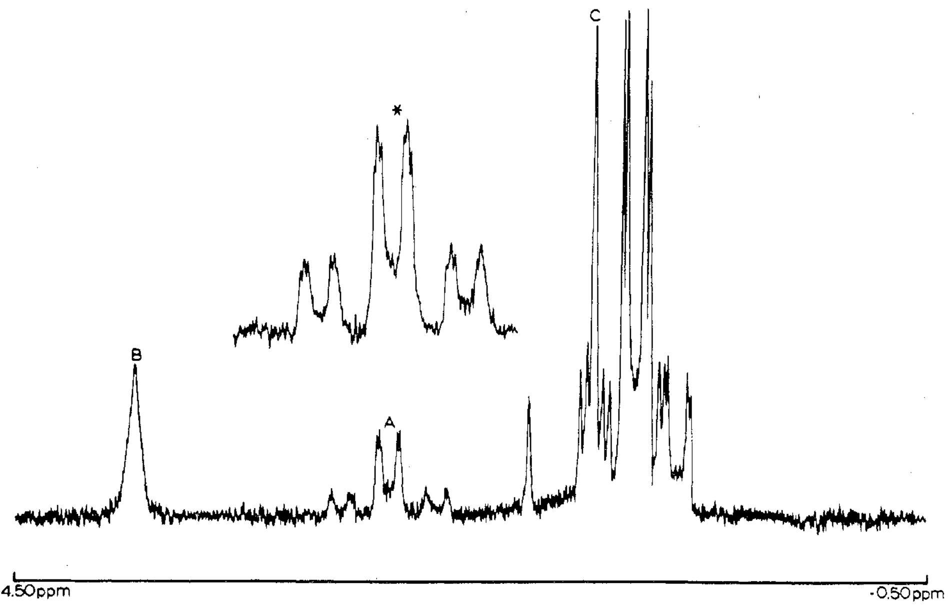
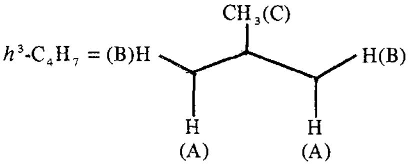


Figure 3. ^{1}H nmr spectrum of $[Pt(h^3\text{-}C_4H_7)\{P(CH_3)_2C_6H_5\}_2]PF_6$ recorded in $CHCl_3$ solution at 30°, 100 MHz. $J(A-B) \approx 0.6$ MHz



methylene groups. The spectrum indicates that coordination to platinum involves *only one* of the allene π orbitals and that within the nmr time scale the allene is not fluxional; *cf.*[47,48] $(CO)_4Fe\{\pi\text{-}(CH_3)_2C{=}C{=}C(CH_3)_2\}$.

The complex II, un = $CH_2{=}CHCH{=}CH_2$, was insufficiently soluble in CD_2Cl_2 and $CHCl_3$ for nmr studies, while in acetone-d_6 dissociation occurred according to eq 2. However, in the presence of free 1,3-butadiene, solubility of this complex is enhanced and the nmr data reported in Table II pertain to a CD_2Cl_2 solution of II, un = $CH_2{=}CHCH{=}CH_2$, containing approximately a 5 molar ratio of excess 1,3-butadiene. Under these conditions, exchange between the coordinated and free diene was slow (by the nmr time scale), and, furthermore, no fluxional character of the coordinated diene was observed. Thus, the properties of this complex *in solution* closely parallel those of other monoolefin complexes II although the anomalous solubility of II, un = $CH_2{=}CHCH{=}CH_2$, may result from a different molecular structure in the solid state.[49] Significantly,[50] chloroform solutions of II, un = $CH_2{=}CHCH{=}CH_2$, in the presence of excess diene do not lead (even at ±60°) to π-allylic platinum cations by insertion into the methylplatinum bond.

The vinylic protons of II, un = $CH_2{=}CHCH_2NH_2$, absorb close to those of the free olefin and furthermore show no coupling to ^{195}Pt. Thus, the ^{1}H nmr data and vibrational spectra are consistent with the amino group being bound to platinum.

π-Allylic Complexes. The ^{1}H nmr of $[Pt(h^3\text{-}C_4H_7)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ is shown in Figure 3. The phosphine methyl proton resonances appear as two sets of overlapping doublets and thus indicate (i) cis phosphine ligands and (ii) the absence of a plane of symmetry about the PtP_2 plane. The spectrum (Figure 3) is independent of temperature, −90 to +60°, and, therefore, shows that the π-2-methallyl ligand does not (i) rotate about the PtP_2C_2 axis,[51-53] (ii) undergo a π-σ (or h^3-h^1) equilibrium,[54,55] (iii) undergo rotation of the terminal CH_2 groups about the carbon-carbon bond while as a whole the π-allyl group retains the π configuration relative to metal,[56] or (iv) undergo a flipping motion,[57] in which the allyl group rotates backward, the central allylic carbon moving away from the metal. Furthermore, addition of CO or pyridine to a chloroform solution of $[Pt(h^3\text{-}C_4H_7)Q_2]^+$ does not change this situation in the temperature range −60 to +60°. Thus the π-allylic ligand is strongly and rigidly bound to platinum (in marked contrast to II, un = olefins which undergo facile rotation and displacement) and shows similar properties to $[\{(C_6H_5)_2P(CH_2)_2\}Pd(h^3\text{-}C_4H_7)]^+$.[58]

The methyl proton resonances of the π-pentamethallyl

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(47) F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968), and references therein.

(48) R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, 89, 2231 (1967).

(49) Some form of intermolecular association involving the butadiene ligand cannot be overruled although the direct analogy of the $[Pt_2Cl_6(C_4H_6)]^-$ structure [V. C. Adam, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Chem. Commun.*, 467 (1971)] can be dismissed on the basis of (i) analytical data and (ii) the fact that dissociation according to eq 2 shows a Pt:C_4H_6 ratio of 1:1.

(50) This contrasts with hydridoplatinum cations *trans*-$[PtH(CH_2{=}CHCH{=}CH_2)Q_2]^+$ which undergo facile Pt-H insertion reactions to give π-allylic complexes: H. C. Clark and H. Kurosawa, unpublished results.

(51) K. C. Ramey and G. L. Statton, *J. Amer. Chem. Soc.*, 88, 4387 (1966).

(52) K. Vrieze, P. Cossee, A. P. Pratt, and C. W. Hibers, *J. Organometal. Chem.*, 11, 353 (1968).

(53) A. Davison and W. C. Rode, *Inorg. Chem.*, 6, 2124 (1967).

(54) J. C. W. Chien and H. C. Dehm, *Chem. Ind. (London)*, 745 (1961).

(55) K. Vreize, A. P. Pratt, and P. Cossee, *J. Organometal. Chem.*, 12, 533 (1968).

(56) J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 302 (1966).

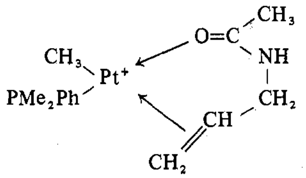
(57) F. A. Cotton, J. W. Fuller, and A. Musco, *Inorg. Chem.*, 6, 179 (1967).

(58) D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 92, 3031 (1970).

ligand are partly obscured by the phosphine methyl proton resonances and, even by a comparison of spectra obtained at 60, 100 and 220 MHz, a definite assignment is not possible.

$[Pt(h^5\text{-}C_5H_5)\{P(CH_3)_2C_6H_5\}_2]PF_6$. The cyclopentadienyl protons appear as 1:2:1 triplets with platinum satellites in the temperature range +30 to −90° consistent with either a pentahapto or a fluxional trihapto or monohapto structure.[47] The stability of the h^3-allylic platinum cations in which platinum attains a 16-electron valence shell and retains a quasi-square-planar geometry[59] *vs.* the attainment of the 18-electron configuration by the adoption of an unusual geometry makes this compound particularly appealing for single-crystal X-ray analysis.[60] Although the vibrational spectrum of this compound is uninformative about the nature of the cyclopentadienyl ligand,[61] a possible distinction between the h^3 and h^5 structures may be indicated by the nature of the phosphine methyl proton resonances. The h^3 structure requires a P-Pt-P angle of *ca.* 90° while the h^5 structure would accomodate a considerably larger angle, $90° < \text{P-Pt-P} < 120°$. The ^{1}H nmr spectrum of the phosphine methyl groups in $[Pt(C_5H_5)Q_2]^+$, shown in Figure 4, is unlike that observed for trans or cis phosphine ligands (compare Figures 1 and 3) or that observed for trigonal platinum(0) as in $Pt(P(CH_3)_2C_6H_5)$.[62] The phosphine methyl pattern (Figure 4) is, however, similar to that of $[PtCF_3\{C_4(CH_3)_4\}\{P(CH_3)_2C_6H_5\}_2]^+$ in which platinum attains an 18-electron configuration by the adoption of an unusual geometry in which the P-Pt-P angle is 96°.[63] Thus left to the sporting method we favor a pentahapto structure with a P-Pt-P angle of *ca.* 105°.

$[PtCH_3\{P(CH_3)_2C_6H_5\}(CH_3CONHCH_2CH{=}CH_2)]PF_6$. The low solubility of this compound precluded a detailed interpretation of the ^{1}H nmr spectrum and hence precludes a positive structural assignment. However, the structure shown next is favored for the following reasons. (1) The large value of ^3J(Pt-H) for the phosphine methyl protons is



consistent with the weak trans influence of a trans oxygen donor.[64] (2) ^2J(Pt-H) and ν_{str}(Pt-C) for the platinum methyl group are consistent with either N or C=C as the trans ligand.[21] (3) The reduction of ν_{str}(C=O) is consistent

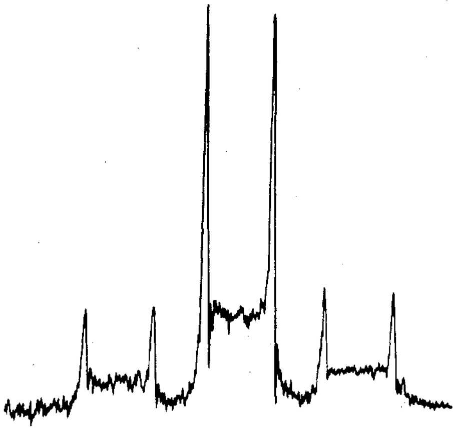


Figure 4. ^{1}H nmr spectrum of the phosphine methyl protons in $[C_5H_5Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ recorded in CD_2Cl_2 at 30°, 100 MHz.

with coordination *via* O and not N. (4) Further indirect support for O donation comes from the spectral properties of the closely related cation *trans*-$[PtCH_3(OCHN(CH_3)_2)Q_2]^+$—see below. (5) Coordination of the olefinic group is supported by the absence of a band assignable to the free olefin in either the infrared or Raman spectrum.

The attempted preparation of *trans*-$[PtCH_3(CH_3CONHCH_2CH{=}CH_2)Q_2]PF_6$ was prompted by the desire to see which atom groups, O, N, or C=C, coordinated preferentially to the $[PtCH_3Q_2]^+$ cation. Previously,[21] we have shown that although the trans-influence series is $C{=}C(\pi) > N(sp, sp^2, \text{ or } sp^3) > O(sp, sp^2, sp^3)$ the thermodynamic stability of the cations results in coordination of N > C=C > O. The allylacetamide ligand was therefore of particular interest since the resonance structure $RN^+H{=}CH{-}O^-$ enhances the nucleophilicity of oxygen at the expense of nitrogen. The resultant displacement-disproportionation reaction, $2[PtCH_3(CH_2{=}CHCH_3NH(OCH_3))Q_2]^+ \rightarrow [PtCH_3Q_2]^+ + [PtCH_3Q(CH_2{=}CHCH_2COCH_3)]^+$, demonstrates that even displacement of a strongly bound phosphine ligand may occur if chelation is possible.

***trans*-$[PtCH_3\{OCHM(CH_3)_2\}Q_2]PF_6$.** The spectral properties of *trans*-$[PtCH_3OCHN(CH_3)_2Q_2]^+$ clearly show that the formamide ligand is O bound: for the methylplatinum group $^2J_{(Pt-H)} = 88$ Hz and ν_{str}(Pt-C) is 576 cm^{-1}; *cf.*[19] *trans*-$[PtCH_3(\text{acetone})Q_2]PF_6$. Previous findings of Gillespie and Birchall[65] have shown that in protic solution $(CH_3)_2NCHO$ is O protonated and thus coordination *via* oxygen is consistent with our previous statements[19-21] regarding the electrophilic character of the cation $[CH_3PtQ_2]^+$.

Comparative Reactivity. Our results suggest that olefins are less susceptible to nucleophilic attack by polar protic solvents than acetylenes when coordinated to the $[CH_3PtQ_2]^+$ cation. However, this could largely be due to the differing thermodynamic stability of the products: acetylenes can yield alkoxycarbene, acetylide, cyclobutadiene, or vinyl ether complexes while olefins can only lead to platinum alkyl derivatives. Exceptions to this are reactions of allenes and cyclopentadiene which lead to "unsaturated" organoplatinum cations. Significantly in this respect, prolonged reaction of allene with *trans*-$PtClCH_3Q_2$ in methanol sol-

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[59] Unusual for Pt(II); *e.g.*, see F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry," 3rd ed., Interscience, New York, N. Y., 1972, p 1031.

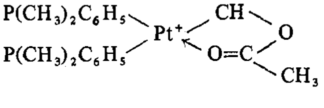
[60] It should be noted that there are to date no examples of truly *trihapto*cyclopentadienylmetal complexes known although the existence of severely tilted ringed complexes is well established: F. A. Cotton, *et al.*, *J. Amer. Chem. Soc.*, 91, 2528 (1969).

[61] Previously reported for similar complexes $Pt(C_5H_5)X(PR_3)_2$ where X = Cl, Br, BF$_4$: R. J. Cross and R. Wardle, *J. Chem. Soc. A.*, 2000 (1971).

[62] H. C. Clark and K. Itoh, *Inorg. Chem.*, 10, 1707 (1971).

[63] M. H. Chisholm, H. C. Clark, D. B. Crump, and N. C. Payne, submitted for publication.

[64] *Cf.*



from H. C. Clark and H. Kurosawa, *J. Chem. Soc., Chem. Commun.*, 150 (1972).

[65] R. J. Gillespie and T. Birchall, *Can. J. Chem.*, 41, 148 (1963). The same conclusion was reached on the basis of ^{14}N line widths: D. Herbison-Evans and R. E. Richards, *Trans. Faraday Soc.*, 58, 845 (1962).

vent led, in addition to $Pt(\pi\text{-}C_4H_7)ClQ_2$ expected from a cationic mechanism involving *trans*-$[PtCH_3(\pi\text{-allene})Q_2]^+$, to the neutral vinyl ether complex *trans*-$PtCl(C(CH_3){=}CH(OCH_3))Q_2$.[66]

It is interesting at this point to compare the reactivities of $[CH_3PtQ_2]^+$ and $[HPtQ_2]^+$ cations. First, the hydride cations $[HPtQ_2]^+$ are the more reactive toward insertion reactions. This may be partly attributable to the thermodynamic properties of the Pt-H bond compared with those of the Pt-C bond either in the $[CH_3PtQ_2]^+$ cation or in the products. Second, the difference in reactivity may relate to the availability of alternative reaction mechanisms. Thus reactions involving $[CH_3PtQ_2]^+$ proceed in a Markownikov manner by electrophilic attack of Pt^+; for example, as mentioned above, $[Pt(h^3\text{-2-methallyl})Q_2]^+$ is formed from reaction of allene with *trans*-$[PtCH_3(acetone)Q_2]^+$ whereas the analogous 1,3-butadiene cation does not lead to a π-allylic derivative by $Pt{-}CH_3$ insertion. In contrast, $[MPtQ_2]^+$ can react by either a Markownikov or an anti-Markownikov mechanism, *i.e.* Pt^+ or H^+ attack of the unsaturated ligand.[67] A consequence of this apparent versatility is the formation of π-allylic complexes from both allenes and 1,3-dienes with $[HptQ]^+$; moreover, this versatility is responsible for the characteristic isomerization and H-D exchange reactions of olefins with platinum hydrides.[67]

Experimental Methods

General methods have been outlined previously.[17]

The general procedure for the preparation of *trans*-$[PtCH_3(un)Q_2]PF_6$ from *trans*-$[PtCH_3(acetone)Q_2]PF_6$ and un parallels the previous preparation[16] of cationic acetylenic complexes, I, and needs no further comment, save to emphasize the advantage of working in a "noncoordinating" solvent such as methylene dichloride.[21] *trans*-$[PtCH_3(acetone)Q_2]PF_6$ was prepared by the previously described method.[19] Gaseous olefins, dienes, vinyl ethers, and allene were obtained from Matheson; other unsaturated ligands were from the Aldrich Chemical Co. Ltd. and were used without further purification. Purification of the complexes reported here, by short column chromatography and repeated recrystallization, follows that reported for the preparation of I.

The low solubility of $[PtCH_3(CH_2{=}CHCH_2NHCOCH_3)Q]PF_6$ allowed easy separation from the more soluble $[PtCH_3Q_2]PF_6$ in the reaction of allylacetamide with *trans*-$[PtCH_3(acetone)Q_2]PF_6$.

Registry No. *trans*-$[PtCH_3(CH_3COCH_3)Q_2]PF_6$, 36523-59-8; *trans*-$[PtCH_3(CH_3COCH_3)A_2]PF_6$, 38466-92-1; *trans*-$[PtCH_3(CH_2{=}CH_2)Q_2]PF_6$, 38466-79-4; *trans*-$[PtCH_3(CH_3CH{=}CH_2)Q_2]PF_6$, 38466-80-7; *trans*-$[PtCH_3(CH_2{=}C{=}CH_2)Q_2]PF_6$, 38466-81-8; *cis*-$[Pt(\pi\text{-}C_4H_7)Q_2]PF_6$, 38466-82-9; *cis*-$[Pt(\pi\text{-}C_8H_{15})Q_2]PF_6$, 38466-83-0; *cis*-$[Pt(\pi\text{-}C_4H_7)A_2]PF_6$, 38466-84-1; $[PtCH_3(CH_3CONHCH_2CH{=}CH_2)Q]PF_6$, 38466-85-2; *trans*-$[PtCH_3(CH_2{=}CHCH{=}CH_2)Q_2]PF_6$, 38466-86-3; *trans*-$[PtCH_3(CH_2{=}CHOCH_3)Q_2]PF_6$, 36548-52-4; *trans*-$[PtCH_3(CH_2{=}CHOC_2H_5)Q_2]PF_6$, 38466-88-5; *trans*-$[PtCH_3(CH_2{=}CHCH_2OH)Q_2]PF_6$, 38466-89-6; *trans*-$[PtCH_3(CH_2{=}CHCH_2NH_2)Q_2]PF_6$, 38585-01-2; $[Pt(\pi\text{-}C_5H_5)Q_2]PF_6$, 38466-90-9; *trans*-$[PtCH_3(OHCNMe_2)Q_2]PF_6$, 38466-93-2.

Acknowledgments. We are grateful to the National Research Council of Canada for financial support.

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[66] T. G. Appleton, private communication.

[67] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 11, 1276 (1972), and work submitted for publication.

Contribution from the Department of Chemistry,
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Interaction of Multidentate Cobalt(II)-Chelate Complexes with Ferricyanide Ion.[1]
I. $Co^{II}EDTA$ and $Co^{II}CyDTA$

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A cyanide-bridged intermediate is formed between $CoCyDTA^{2-}$ and $Fe(CN)_6{}^{3-}$ in a manner exactly analogous to that for the $CoEDTA^{2-}{-}Fe(CN)_6{}^{3-}$ reaction

$$CoY^{2-} + Fe(CN)_6{}^{3-} \overset{K_1}{\rightleftharpoons} [Y{-}Co^{III}{-}CN{-}Fe^{II}(CN)_5]^{5-} \xrightarrow{k_3} CoY^- + Fe(CN)_6{}^{4-}$$

The values of K_1, k_1, and k_3 at 25° (pH 5.00, $I = 0.66\ M$ with acetate, acetic acid) are 831 M^{-1}, $8 \times 10^4\ M^{-1}\ sec^{-1}$, and $5.40 \times 10^{-3}\ sec^{-1}$ for $CoEDTA^{2-}$ and 43.6 M^{-1}, $3.58 \times 10^3\ M^{-1}\ sec^{-1}$, and $2.21 \times 10^{-2}\ sec^{-1}$ for $CoCyDTA^-$. Activation parameters are reported. The rate and equilibria data are readily understood on the basis of the steric hindrance suffered by the pendant acetate group in moving aside to allow the entry of the cyano group into the inner coordination sphere of the cobalt complex.

Mechanisms of electron-transfer reactions between inorganic complex ions in solution encompass a substantial segment of current research activity. Of particular interest has been the inner-sphere mechanism[2] in which the transfer of an electron is an intramolecular event. Of the wide variety of inorganic and organic ligands used, the cyano group provides an interesting example of a bridging ligand since it offers the opportunity for simultaneous carbon bonding to one metal ion and nitrogen bonding to the other. A number of inner-sphere reactions involving cyano bridging have been reported in the literature.[3] In reactions of this type, when at least one of the product ions is substitution labile, the decomposition (or dissociation) of the successor binuclear complex is rapid, and conclusions concerning the structure and reactiv-

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[1] Presented in part before the Division of Inorganic Chemistry, Symposium on Multistep Redox Reaction Mechanisms, Second Northeast Regional Meeting of the American Chemical Society, Providence, R. I., Oct 1970.

[2] H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

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