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Redox, Ligand-Exchange, Oligomerization, and Hydrosilation Chemistry of *trans*-Dichloro(ethylene)(phenazine)platinum

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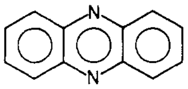
A series of compounds of the type *trans*-(amine)$PtCl_2(C_2H_4)$ (amine = phenazine, quinoxaline, pyrazine, phenazine *N*-oxide, 2,6-dimethylpyrazine, tetramethylpyrazine, acridine) was prepared by displacement of chloride from $PtCl_3(C_2H_4)^-$. (phenazine)$PtCl_2(C_2H_4)$ is an effective hydrosilation catalyst. It reacts with L (L = styrene, Ph_3P, Ph_3As) to form (phenazine)$PtCl_2L$ and (phenazine)$[PtCl_2L]_2$. Pyrolysis leads to $(phenazine)_2(PtCl_2)_2(C_2H_4)$. Reduction of (phenazine)$PtCl_2(C_2H_4)$ to form $[(phenazine)PtCl_2(C_2H_4)]_2^{-\cdot}$, whose ESR spectrum is discussed, was found by double-potential-step chronocoulometry to proceed by an ECE mechanism. The platinum-catalyzed reduction by hydrogen yields $H[(phenazine)PtCl_2(C_2H_4)]_2$. Reduction by silanes, R_3SiH, in $CHCl_3$ produces $H_3[(phenazine)PtCl_2(C_2H_4)]_3PtCl_3$. Characterization of these compounds by X-ray photoelectron spectroscopy is discussed.

Introduction

Transition-metal complexes of electroactive ligands, that is, organic molecules that can undergo reversible electron-transfer processes, constitute an important area of chemistry on account of the predictably complex behavior of materials containing multiple redox-active centers. This importance is reflected, for example, in metalloenzymes and has general implications for catalytic processes. Organic heterocycles, especially those having one or more annelated aromatic rings, form a broad class of electroactive ligands, and we have previously described phenazine coordination compounds containing Rh(I) and Ir(I)[1] as well as partially oxidized phenoselenazine and phenothiazine complexes of Pt(II).[2] In this paper, we describe the chemistry of (phz)$PtCl_2(C_2H_4)$ (phz = phenazine) and of related compounds of the type (amine)$PtCl_2$(olefin) in which the amine is an electroactive heterocyclic ligand. This material is a very efficient hydrosilation catalyst[3] and is the source of a series of novel bimetallic platinum–phenazine complexes and of polymetallic reduction products which are accessible by electrochemical routes or by reaction with dihydrogen or silanes.

Synthetic Chemistry

In this work, the principal heterocyclic nitrogen donors employed are phenazine (**1**), quinoxaline (quinox, **2**), pyrazine (pyr, **3**), and phenazine *N*-oxide (phz *N*-ox, **4**). Structure and bonding in pyridine (py) and pyridine *N*-oxide (py *N*-ox) $PtCl_2$(olefin) complexes have been extensively studied,[4-12] and it has been recognized that the Pt–N bond strength can be affected by electronic interactions with para substituents on the pyridine ring. Chottard, Mansuy, and Bartoli[13] found that ortho substitution by methyl groups on the coordinated pyridine in *trans*-(pyridine)$PtCl_2(C_2H_4)$ led to an increase in stability of the nitrogen donor to ligand displacement. Pyridine has been shown to be more labile than ethylene.[12] The crystal structure of $(2,4,6\text{-}Me_3py)PtCl_2(C_2H_4)$ demonstrated a significant twisting of the aromatic ring out of the $PtCl_2$ plane; this arrangement probably represents a compromise between minimization of nonbonded CH_3–Cl repulsions and maximization of overlap between the Pt 5d and aromatic π orbitals.[14] It is well-known that olefins coordinated to Pt(II) exert a strong trans effect, chloride trans to ethylene in $PtCl_3(C_2H_4)^-$ being readily displaced by other ligands, L, to give *trans*-$LPtCl_2(C_2H_4)$. Often, for example when L is triphenylphosphine, the rate of subsequent displacement of ethylene is very fast and only the bis(ligand) derivative, $(Ph_3P)_2PtCl_2$, can be isolated. In other cases, for example when L is pyridine or pyrazine, either $LPtCl_2(C_2H_4)$ or L_2PtCl_2 can be isolated, depending, on reaction conditions. We find that if suitable, bulky planar ligands, such as phenazine, are employed, this reaction produces only (phz)$PtCl_2(C_2H_4)$ (**5**). Similarly, treatment of $KPtCl_3(C_2H_4)$ with 1 equiv of **2**, **3**, **4**, 2,6-dimethylpyrazine and 2,3,5,6-tetramethylpyrazine in acetonitrile produces (quinox)$PtCl_2(C_2H_4)$ (**6**), (pyr)$PtCl_2(C_2H_4)$ (**7**), (phz *N*-ox)$PtCl_2(C_2H_4)$ (**8**), $(2,6\text{-}Me_2pyr)PtCl_2(C_2H_4)$ (**9**), and $(2,3,5,6\text{-}Me_4pyr)PtCl_2(C_2H_4)$ (**10**), respectively.[15]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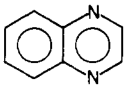
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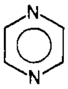
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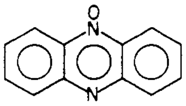
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(phz)$PtCl_2(C_2H_4)$ exhibits a surprising resistance to displacement of ethylene by other nucleophiles, unusual thermal stability relative to that of analogues made from sterically unencumbered ligands, and high kinetic stability in solution. It is probable that this enhanced stability is due primarily to steric effects as can be seen by inspection of molecular models. A scale model of (phz)$PtCl_2(C_2H_4)$ was constructed that incorporated (1) trans arrangement of the two chlorine ligands, justified by the observation of only one Pt–Cl stretching band in the infrared spectrum at 340 cm^{-1}, and (2) the usual η^2 ethylene–platinum bonding arrangement, justified by the $^{195}Pt-^{13}C$ and $^{195}Pt-C-^{1}H$ coupling constants of 166 and 63 Hz, respectively. This model reveals that nonbonded interactions between the chlorine atoms and the

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Table I. Thermal Programmed Desorption Data

	T_{max}, °C	
compd[a]	heterocycle	C_2H_4
(phz)PtCl$_2$(C$_2$H$_4$)	260	260, 300[b]
(quinox)PtCl$_2$(C$_2$H$_4$)	242	260
(pyr)PtCl$_2$(C$_2$H$_4$)	180	170, 245[b]
(phz *N*-ox)PtCl$_2$(C$_2$H$_4$)	310	230
(2,6-Me$_2$pyr)PtCl$_2$(C$_2$H$_4$)	310	165
(2,3,5,6-Me$_4$pyr)PtCl$_2$(C$_2$H$_4$)	185	180
(py)PtCl$_2$(C$_2$H$_4$)	295	175, 225[b]
(acd)PtCl$_2$(C$_2$H$_4$)	335	265, 285[b]

[a] Legend: phz, phenazine; quinox, quinoxaline; pyr, pyrazine; py, pyridine; acd, acridine. [b] Bimodal distribution.

Table II. Carbonyl Stretching Frequencies in LPtCl$_2$(CO)

L	ν_{CO}, cm^{-1}	L	ν_{CO}, cm^{-1}
pyrazine	2137	2,6-dimethylpyrazine	2135
quinoxaline	2135	2,3,5,6-tetramethylpyrazine	2130
phenazine	2132	acridine	2128
phenazine *N*-oxide	2132	pyridine	2128

phenazine peri hydrogens force the heterocyclic ligand to twist so that its molecular plane is approximately perpendicular to that defined by the PtCl$_2$ unit. In this configuration, the phenazine and ethylene π^* orbitals are orthogonal. Because the two unsaturated ligands do not compete for the same metal 5d electrons to achieve back-bonding, the phenazine–Pt and ethylene–Pt bonds are expected, and found, to be stronger than they would otherwise be in the absence of this effect. The sterically induced twisting of the phenazine ligand thus leads to a decreased reactivity of **5** and its analogues with species with which it might react by a dissociative mechanism. Furthermore, with phenazine in a twisted or rotated configuration, the peri hydrogens can be seen from the model to block the axial fifth and sixth coordination sites at platinum. This is expected to lead to decreased activity toward attacking reagents that react by a bimolecular, associative mechanism, the most probable alternative route by which ligand displacements at Pt(II) occur. Thus, ethylene in **5** is not displaced by additional **1** whereas **7** reacts with additional pyrazine to form *trans*-(pyr)$_2$PtCl$_2$ (**11**). Mere use of bulky ligands in the preparative reactions is insufficient to lead to a similar effect or even to control the stoichiometry. For example, from the reaction of KPtCl$_3$(C$_2$H$_4$) with 1 equiv of triphenylphosphine, tri-*o*-tolylphosphine, and tri-*o*-tolyl phosphite, (Ph$_3$P)$_2$PtCl$_2$, [(C$_7$H$_7$)$_3$-P]$_2$Pt$_2$Cl$_4$, and [((*o*-tol)O)$_3$P]$_2$PtCl$_2$ (tol = tolyl) respectively are obtained. Use of phenothiazine (psz), which has a geometry superficially similar to that of phenazine, affords only (psz)$_2$PtCl$_2$9[2] This donor molecule is folded along the S–N vector so that the peri hydrogens do not inhibit close approach of additional ligands.

Objective evidence for enhanced stability of the new (heterocycle)PtCl$_2$(C$_2$H$_4$) compounds was obtained from both solid- and solution-phase experiments. The temperature at which ethylene and the ligand are released from the solid complexes was assessed by thermal programmed mass spectrometry. In this technique, the ion currents for the parent ions derived from C$_2$H$_4$ and the heterocyclic ligand are followed as a function of temperature as the sample is heated. The temperature at which the maximum ion current occurs, T_{max}, is related to the dissociation energy for a first-order process, E_d, by

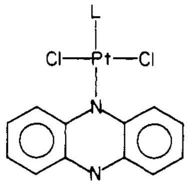
$$E_d/RT_{max} = \ln (\nu T_{max}/\beta) - \ln (E_d/RT_{max})$$

where β is the heating rate and ν is the preexponential factor.[16] Thus, T_{max} may be taken to be a measure of the Pt–ligand bond strength. Typical data are shown in Table I. While a detailed discussion of the results is not warranted at this time, significant increases in thermal stability of (phz)PtCl$_2$(C$_2$H$_4$), in which the nitrogen-containing ligand is considered to be twisted for the same reason as phenazine is, relative to that of (pyr)PtCl$_2$(C$_2$H$_4$) and of (acd)PtCl$_2$(C$_2$H$_4$) (acd = acridine) relative to that of (py)PtCl$_2$(C$_2$H$_4$) are readily apparent.

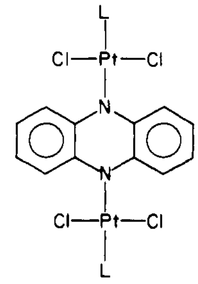
In chloroform solution, *trans*-LPtCl$_2$(C$_2$H$_4$) (L = pyrazine, quinoxaline, and phenazine) are monomeric and not significantly dissociated as judged by vapor pressure osmometry (cf. Table S-1). The ^{1}H and ^{13}C NMR spectra[17] of the twisted phenazine complex, **5**, reveal no exchange or dissociation phenomena. On the other hand, the ^{1}H NMR spectrum of (quinox)PtCl$_2$(C$_2$H$_4$), in which compound steric repulsions are reduced because it has one fewer peri hydrogen, shows that the quinoxaline is undergoing rapid intermolecular exchange, since down to −73 °C, it has the same symmetry as the free ligand and does not exhibit ^{1}H–^{195}Pt coupling. The ethylene, however, remains attached to platinum. Pyrazine is an even less bulky ligand than quinoxaline as it has no peri hydrogens. In (pyr)PtCl$_2$(C$_2$H$_4$), both pyrazine and ethylene participate in rapid intermolecule exchange at room temperature as the protons in both ligands are not spin coupled to ^{195}Pt.[17] These data indicate that, as steric repulsions in LPtCl$_2$(C$_2$H$_4$) are reduced by successive removal of the annelated rings containing peri hydrogens, kinetic lability of both the ligand and ethylene increases. This conclusion is supported by infrared studies of LPtCl$_2$CO. These compounds are prepared by treating the corresponding ethylene complexes **5**–**10** with excess carbon monoxide. The carbonyl stretching frequencies in these compounds fall within a 9-cm^{-1} range (Table II). This suggests that the electron densities on platinum as probed by this $D_{\infty h}$ ligand, are all very similar and that large differences in chemical behavior are attributable largely to steric effects.

Ligand Exchange Reactions

Displacement of ethylene by styrene in (py)PtCl$_2$(C$_2$H$_4$) proceeds rapidly at room temperature. In contrast, (phz)PtCl$_2$(C$_2$H$_4$) is more robust and its reaction with excess styrene is only about 70% complete after 0.5 h at 30 °C and higher temperatures are required to force the olefin replacement to completion. Reaction of **5** with styrene (excess), triphenylphosphine, triphenylarsine, and diethyl sulfide (excess) in refluxing benzene affords (phz)PtCl$_2$L (**13**, L = PhCH═CH$_2$; **14**, L = Ph$_3$P; **15**, L = Ph$_3$As; **16**, L = Et$_2$S). These hydrocarbon-soluble yellow compounds have chemical and spectroscopic properties similar to those of **5**; only one Pt–Cl stretching band is observed, indicating retention of the trans stereochemistry, and the peri protons are significantly deshielded as they are in **5** for the same reason. Produced as insoluble byproducts by an apparent disproportionation reaction are the bright orange complexes (phz)[PtCl$_2$L]$_2$ (**17**, L = PhCH═CH$_2$; **18**, L = Ph$_3$P; **19**, Ph$_3$As), which are formulated as bimetallic phenazine complexes in which a *trans*-PtCl$_2$L unit is attached to each donor nitrogen. The electronic spectra of **17**–**19** (cf. Table III) show bands at ca. 480 and 550 nm, which are not observed in the spectra of the monometallic analogues **13**–**15**. Balch and Cooper[18] have established that the electronic spectra of ligand-bridged, planar Rh(I) complexes are sensitive to the separation between the metal centers and the relative orientation of their



13, L = PhCH═CH$_2$
14, L = Ph$_3$P
15, L = Ph$_3$As
16, L = (C$_2$H$_5$)$_2$S



17, L = PhCH═CH$_2$
18, L = Ph$_3$P
19, L = Ph$_3$As

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Table III. Electronic Spectra

compd	λ_{max}, nm (log ϵ)[a]
5	251 (4.83), 257 (4.82), 360 (4.00), 365 (sh), 376 (4.17), 403 (sh), 427 (3.51)
6	323 (3.84)
7	272 (3.79), 320 (3.12)
8	260 (4.50), 270 (4.76), 278 (4.73), 333 (3.51), 347 (3.70), 366 (3.86), 385 (4.02), 423 (3.85), 442 (3.83), 464 (3.70)
9	253 (3.66), 290 (sh), 296 (3.89)
10	241 (3.52), 282 (3.89)
11	260, 355, 390[b]
12	254 (4.98), 258 (4.91), 326 (3.40), 335 (sh), 340 (3.82), 351 (3.85), 359 (4.12), 375 (3.72), 394 (3.75), 412 (355)
13	258 (4.93), 282 (3.80), 358 (sh), 366 (4.10), 377 (4.21), 405 (3.72), 428 (3.61)
14	255 (4.34), 355 (sh), 364 (3.61), 375 (3.68), 398 (sh), 4.16 (3.16)
15	250 (4.40), 355 (sh), 364 (sh), 375 (3.65), 398 (3.25), 416 (3.17)
16	258 (4.90), 360 (sh), 365 (sh), 377 (4.19)
17	268, 296 (sh), 330 (sh), 400, 480 (sh)[b]
18	270, 308 (sh), 376, 398, 444 (sh), 474, 545[b]
19	264, 380, 390, 415, 480, 550[b]
20	250, 365 (sh), 384, 410, 440[b]
	345 (sh), 355 (sh), 363 (4.09), 374 (4.11), 425 (sh)[c]
21	264, 400[b]
22	265, 400, 508[b]
23	375 (sh), 388 (3.88), 445 (sh), 479 (3.20)
24	376, 446, 548, 586, 660, 690, 728[b]
25	384, 446, 605 (sh), 660, 710, 730[b]
$H_2(phz)^{+\cdot}$	363, 372, 432, 450, 590, 648, 696, 696, 716[d]
$phz^{-\cdot}Na^+$	484, 510, 536, 550, 580, 586[e]

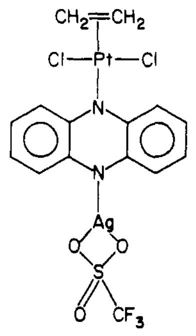
[a] In $CHCl_3$ unless otherwise noted. [b] Nujol mull. [c] Acetone solvent. [d] CF_3CO_2H solvent. [e] THF solvent.

coordination planes. Bathochromic shifts in the low energy MLCT bands of bimetallic compounds of the type $[Rh(CO)Cl(Ph_2P(CH_2)_nPPh_2)]_2$ ($n = 1$–4) are observed when the two metal centers interact.[19] It seems likely that the new long-wavelength bands in **17**–**19** are associated with similar proximity-shifted charge-transfer absorptions due to interaction of the two Pt(II) centers through the bridging phenazine ligand.

X-ray photoelectron spectroscopy (XPS) is quite helpful in confirming the proposed bimetallic structures of **17**–**19**. The N(1s) core level binding energy, E_b, for pure phenazine is 398.7 eV (relative to the C(1s) reference line at 285.0 eV). In phenazine complexes in which only one nitrogen atom is coordinated to a formally divalent transition metal, two N(1s) lines are observed. These occur at 399.4 and 400.4 eV in $(phz)PtCl_2(C_2H_4)$ and at 399.1 and 400.1 eV in $(phz)Pd(C\text{-}F_6acac)(O_2\text{-}F_6acac)$.[20] Similarly, $(quinox)PtCl_2(C_2H_4)$ exhibits two N(1s) lines of equal intensity at 399.5 and 401.0 eV. In the phenazine *N*-oxide complex **8**, the XPS peak at 400.3 eV is assigned to the N–Pt nitrogen and that at 402.8 eV to the nitroxide nitrogen in which the $N^+–O^-$ resonance form having a positive charge on nitrogen contributes to the substantially higher binding energy. The effect of coordination to monodentate phenazine of Pt(II), an electron-withdrawing transition metal, is to raise the N(1s) core level of the ligating nitrogen to ca. 400 eV while E_b for the other nitrogen atom, which is not bonded to a metal, remains relatively unaffected at ca. 399.5 eV. The XPS spectra of **17**–**19** all show a single, sharp (fwhm 1.6 eV) N(1s) line at 400.6 eV, indicating that, in these compounds, a $LPtCl_2$ unit is attached to each nitrogen donor site in phenazine.

Acid–Base and Oligomerization Reactions

Treatment of **5** with silver trifluoromethanesulfonate in benzene affords the 1:1 adduct $(phz)PtCl_2(C_2H_4)\cdot AgCF_3SO_3$ (**20**), whose proposed structure features Pt(II) coordinated to one donor site in phenazine and Ag(I) to the other. In agreement with this, the XPS spectrum of **20** displays a single N(1s) photoemission line at 400.2 eV. In solution, the compound can ionize and the molar conductance of a 1.7×10^{-3} M solution in nitromethane is 57 Ω^{-1} cm^2 mol, consistent with 1:1 electrolyte behavior.[21] The ^{19}F NMR spectrum in acetone shows a singlet at δ −77.6 indicative of ionic behavior and the presence of $CF_3SO_3^-$. Similarly, reaction of **5** with anhydrous hydrogen chloride in dichloromethane affords the hydrochloride salt $[H(phz)PtCl_2(C_2H_4)]Cl$ (**21**) (ν_{NH} (Fluorolube) 2860 cm^{-1}).



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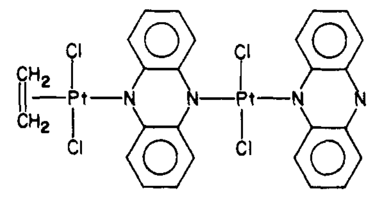
Upon heating of a solution of $(phz)PtCl_2(C_2H_4)$ under nitrogen in refluxing toluene, $(phz)_2Pt_2Cl_4(C_2H_4)$ (**22**) separates as a red, microcrystalline powder. Rigorous physical characterization of this material is impeded by its very low solubility in nonreactive solvents; however, spectroscopic data provide strong evidence that it has the structure shown. The remarkably simple infrared spectrum demonstrates the presence of *trans*-$PtCl_2$ units (ν_{PtCl} 340 cm^{-1}) and shows characteristic phenazine bands at 1525 and 1340 cm^{-1}. The Raman spectrum shows a strong, infrared-inactive band at $\Delta\nu$ 1210 cm^{-1}, which is assigned to C=C stretching in the coordinated ethylene.[22] Neither infrared nor Raman spectra contain bands attributable to Pt–Cl–Pt bridges.



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The visible spectrum of **22** as a Nujol mull shows a low energy MLCT band at 510 nm, which, if the reasoning above is followed, is indicative of a $(phenazine)(PtCl_2L)_2$ unit. Finally, the deconvoluted XPS spectrum discloses two N(1s) peaks at 398.8 and 400.2 eV in a 1:3 ratio. Using the arguments developed above, we assign the former emission line to the uncoordinated nitrogen atom in **22** and the more intense peak at higher binding energy to the three nitrogens coordinated to platinum, which is in agreement with the proposed structure. Thus, the thermally induced aggregation of **5** is distinct from the photochemical reactions of *cis*-(amine)$PtCl_2$(olefin), which, in weakly coordinating solvents, yield dimeric $Pt_2Cl_4(amine)_4$ products having chlorine bridges between the two platinum atoms.[23]

The reaction of **5** with $PPN^+PtCl_3(C_2H_4)^-$ in refluxing chloroform yields $PPN^+(phz)PtCl_3^-$ (**23**) (ν_{PtCl} 320 cm^{-1}) rather than the expected bimetallic products. The electronic spectrum of this compound in chloroform exhibits maxima at 445 (sh) and 470 nm along with a very broad absorption centered at ca. 540 nm, indicating possible aggregation in solution. However, the ^1H NMR spectrum shows that the ratio of deshielded peri protons, δ 10.9, to other aromatic protons is 1:18 as expected.

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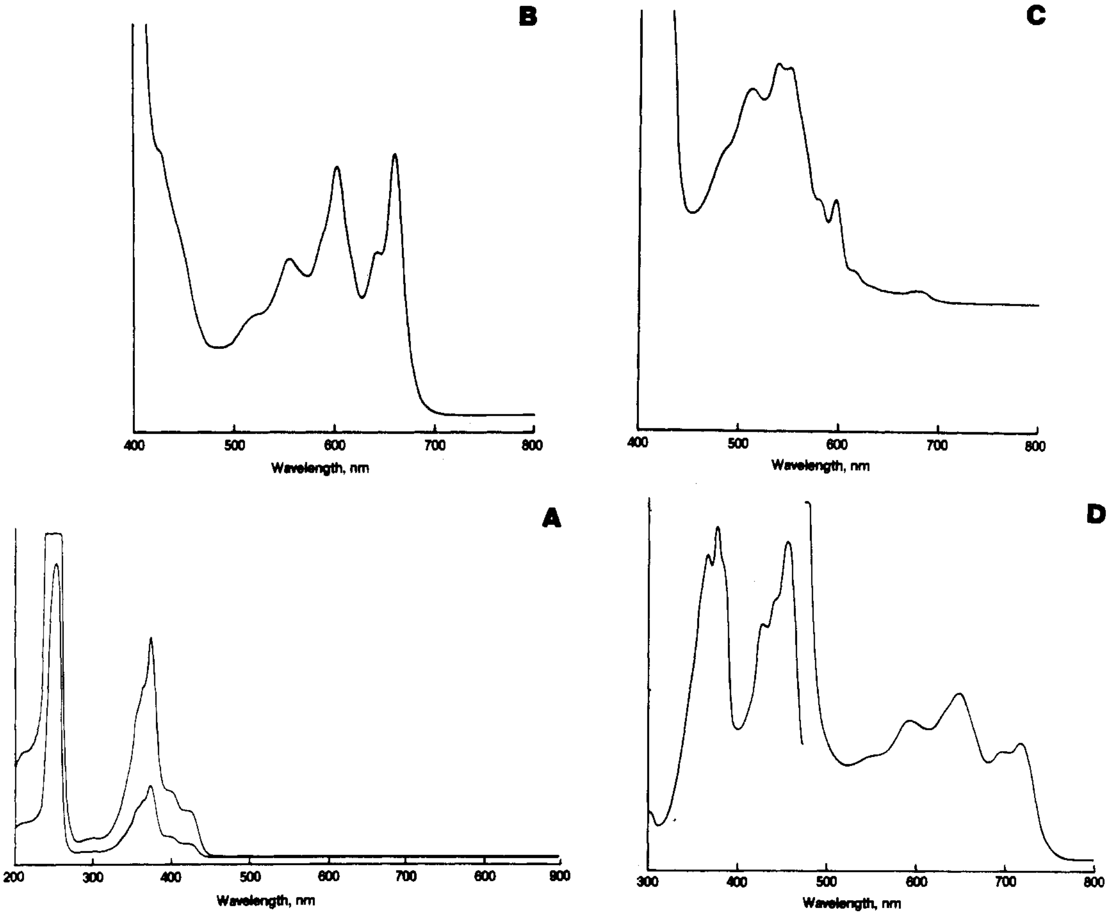

Figure 1. Electronic spectra of (A) $(phz)PtCl_2(C_2H_4)$ in $CHCl_3$, (B) $[(phz)PtCl_2(C_2H_4)]_2^{-}\cdot$ in CH_2Cl_2, (C) $Na^+phz^-\cdot$ in THF, and (D) $H_2(phz)^+\cdot$ in CF_3CO_2H.

Redox Chemistry

Electrochemical reduction of platinum(II) complexes is usually an irreversible two-electron process that leads to metallic platinum.[24] Exceptions occur when the complex contains ligands capable of supporting a delocalized negative charge, such as maleonitriledithiolate.[25] Nonintegral electron transfer has been observed in condensed-phase platinum compounds such as, for example, phthalocyanine–platinum complexes,[26] partially oxidized derivatives of $K_2Pt(CN)_4$,[27] and platinum bronzes.[28] The electrochemical reduction of phenazine in acidic media produces the stable dihydrophenazine catiion radical,[29] and reduction with alkali metals in ethanol solvents[30] or by electrolysis[31] yields the phenazine anion radical. Cyclic voltammetry data for (amine)$PtCl_2(C_2H_4)$ compounds prepared in this work are given in Table IV. With the exception of $(py)PtCl_2(C_2H_4)$, all the compounds studied here by cyclic voltammetry exhibit a one-electron reduction at potentials more positive than those of the irreversible two-electron reductions of $PtCl_4^{2-}$ and $PtCl_3(C_2H_4)^-$ to metallic platinum.

These data strongly suggest that the electron added to (amine)$PtCl_2(C_2H_4)$ (amine = phenazine, quinoxaline, pyrazine, and phenazine *N*-oxide) is extensively delocalized on the heterocyclic ligand. In particular, reduction of $(phz)PtCl_2(C_2H_4)$ yields a novel organometallic anion radical dimer whose properties will be described in this section.

Table IV. Cyclic Voltammetric Data

compd	*E*, V	compd	*E*, V
$(phz)PtCl_2(C_2H_4)$	$-0.730^{a,c}$	phenazine	$-1.28^{a,c}$
$(quinox)PtCl_2(C_2H_4)$	$-0.56^{b,c}$	quinoxaline	$-1.9^{b,d}$
$(pyr)PtCl_2(C_2H_4)$	$-0.78^{b,c}$	pyrazine	$\sim 2.25^{b,d}$
$(py)PtCl_2(C_2H_4)$	none obsd	$(Ph_4As)_2PtCl_4$	$-2.20^{b,d}$
(phz	$-0.60^{b,c}$		$+0.90^{b,e}$
N-ox)$PtCl_2(C_2H_4)$	$-1.08^{b,c}$	$(n\text{-}C_4H_9)_4NPtCl_3(C_2H_4)$	$-2.1^{b,d}$
	$-1.31^{b,d}$		

[a] Conditions: $CH_2Cl_2/(C_4H_9)_4NPF_6$ (0.1 M) solution; AgCl/Ag (1.0 M KCl, saturated AgCl) reference electrode; polished glassy-carbon working electrode; 20 ± 2 °C. [b] Conditions: $CH_2Cl_2/(C_4H_9)_4NClO_4$ (0.2 M) solution; SCE reference electrode; carbon working electrode; 0 ± 2 °C. [c] $(E_{p,c} + E_{p,a})/2$. [d] $E_{p,c}$. [e] $E_{p,a}$.

Cyclic voltammograms of **5** in dichloromethane/$(C_4H_9)_4NPF_6$ at a 50 mV/s scan rate disclose two reduction waves at $E_{p,c} = -0.762$ and -1.3 V vs. a AgCl/Ag reference electrode. The details of the rather complex electrochemistry are discussed below. However, the first wave is quasireversible ($E_{p,a} = -0.698$ V) in that $(i_{p,c}/i_{p,a})$ is 0.95 while the second wave is irreversible ($i_{p,c}/i_{p,a} \simeq 0$). Coulometric studies carried out at potentials cathodic of the first reduction wave reveal that 0.5 electron/platinum are taken up to yield the blue-green radical $[(phz)PtCl_2(C_2H_4)]_2^{-}\cdot$. This radical reacts rapidly with oxygen to regenerate **5**, but solutions in dry, oxygen-free solvents are stable for at least several days at room temperature. Exhaustive reduction cathodic of the second wave consumes 3 electrons/metal and generates phenazine anion radical, identified by its visible and ESR spectra, and metallic platinum. Similarly, reduction with sodium amalgam or sodium naphthalide in dipolar, aprotic solvents such as acetonitrile, tetrahydrofuran and 1,2-dimethoxyethane affords stable solutions of $Na[(phz)PtCl_2(C_2H_4)]_2$. We consider that the nonintegral value for *n* at the first reduction wave is clear evidence for the formation of an anion radical dimer (vide infra). The electronic spectrum

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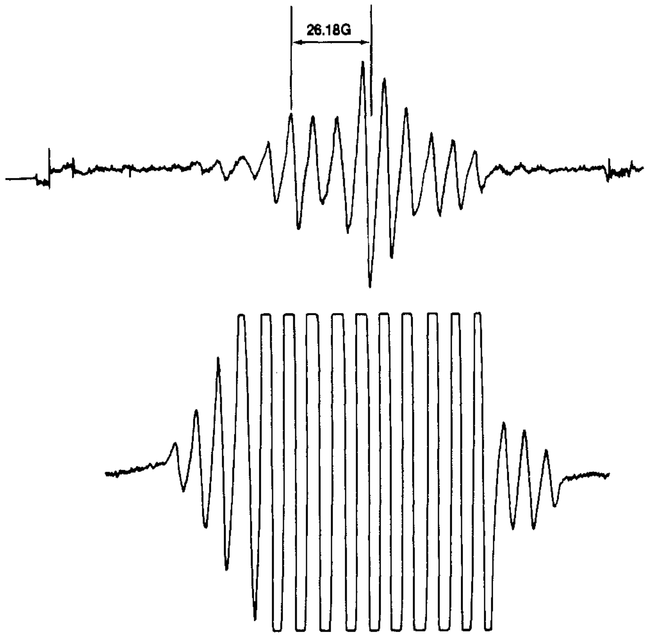

Figure 2. ESR spectrum of $[(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)]_2^{-\cdot}$ at high (lower curve) and low (upper curve) gain. Field marker is the center line from Fremy's salt.

of $[(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)]_2^{-\cdot}$ exhibits bands at 525 (sh), 556 (log ϵ 3.23), 603 (3.43), 642 (3.24) and 660 (3.45) nm (Figure 1) and is distinctly different from that of the dihydrophenazine cation radical. More importantly, the absorptions are shifted by about 200 nm to longer wavelength with respect to phenazine anion radical, $\text{phz}^{-\cdot}$, indicative of more extensive electron delocalization in the dimeric radical.

The electron spin resonance of $[(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)]_2^{-\cdot}$ in fluid solution consists of a symmetrical 17-line pattern (Figure 2). Spectra obtained at high gain do not show any ^{195}Pt satellites or ^1H hyperfine structure; the absence of the latter feature is confirmed by the ESR spectrum of $[(\text{phz-}d_8)\text{PtCl}_2(\text{C}_2\text{H}_4)]_2^{-\cdot}$. The g value in dichloromethane is 2.008, indicating that spin density is located largely on the phenazine rings. A much higher g value and ^{195}Pt hyperfine coupling are to be expected in a metal-centered radical.[2] Computer simulation of the ESR spectra demonstrates that $[(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)]_2^{-\cdot}$ contains two nonequivalent pairs of nitrogen atoms, N(1) and N(2), with ^{14}N hyperfine coupling constants $A_{\text{N(1)}}$ and $A_{\text{N(2)}}$ of 24 and 8 G, respectively. Thus, the ESR data also indicate that the paramagnetic species formed on reduction of **5** is a dimeric anion radical, a conclusion supported by a detailed study, described below, of the electrochemical reduction processes.

The cyclic voltammogram of $(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)$ at low (0.1 mM) concentrations in methylene chloride and at relatively fast (50 mV/s) scan rates between the potential limits +1.80 and −1.10 V exhibits a single quasi-reversible one-electron electrode process with $E^{\circ\prime} = -0.730$ V ($i_{\text{p,a}} - i_{\text{p,c}} = 64$ mV) due to reduction of **5** to $(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)^{-\cdot}$. Either increasing the concentration or decreasing the scan rate results in a systematic decrease in the anodic current due to oxidation of the anion radical to neutral **5** and the appearance of a new anodic peak at $E_{\text{p,a}} \simeq -0.18$ V (cf. Figure 3). These qualitative changes in the cyclic voltammograms are indicative of an EC process which involves reaction of a monomeric anion radical, $(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)^{-\cdot}$, with its neutral precursor. Saveant and co-workers[32] have described a method using cyclic voltammetric data to define the mechanism of such a reaction and to extract the rate constant for the chemical process. The method consists of measuring the shift in $E_{\text{p,c}}$ as a function of log (C^0/v), where C^0 is the bulk concentration of the electrochemically active substrate. A plot of $E_{\text{p,c}}$ vs. log (C^0/v) should

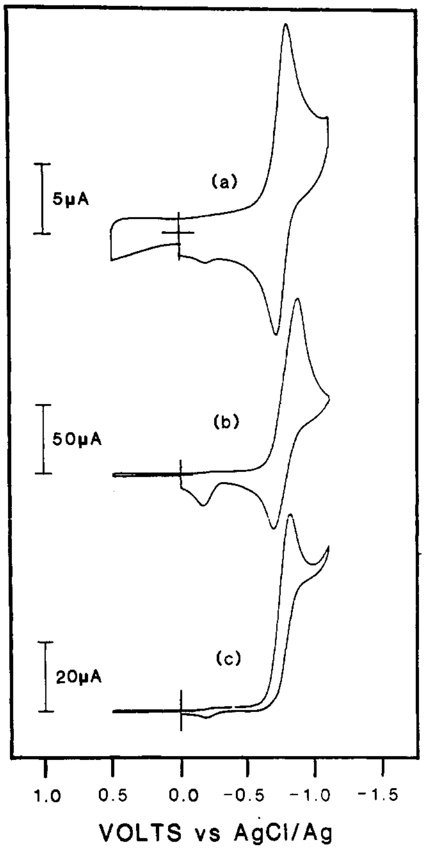

Figure 3. Cyclic voltammograms of $(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)$ in 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ at a 0.4 cm^2 glassy-carbon electrode: (a) 0.17 mM, 50 mV/s; (b) 1.7 mM, 50 mV/s; (c) 1.7 mM, 10 mV/s. All scans were initiated from 0.0 V, scanning toward more positive potentials.

yield a straight line with a slope dependent on the mechanism of the chemical step. Experimentally, we have found that this analysis is unsatisfactory when applied to the $(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)$ system because it assumes a diffusion-controlled heterogeneous electron-transfer rate constant. By measuring the peak separation ($E_{\text{p,a}} - E_{\text{p,c}}$) at low concentrations (in order to avoid interference by the chemical step) as a function of increasing scan rate, we have found that the heterogeneous electron-transfer rate for the electrode process

$$e^- + (\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4) \rightarrow [(\text{phz})\text{PtCl}_2(\text{C}_2\text{H}_4)]^{-\cdot}$$

is substantially below the diffusion limit [($E_{\text{p,a}} - E_{\text{p,c}}$) = 64 mV at 50 mV/s and at 2000 mV/s ($E_{\text{p,a}} - E_{\text{p,c}}$) = 375 mV],[33] thus precluding quantitative use of the Saveant relationship.

Double-potential-sweep chronocoulometry, however, is appropriate for the study of the chemical step in an EC process when the initial electron-transfer step is slow,[34-36] and it is useful for evaluation of both mechanistic details of the chemical reaction step and the rate constant, k, for the reaction. Briefly, the method consists of two charge measurements. In the forward step measurement, the amount of charge passed is measured upon applying a potential step from an initial value ($E_0 = -0.30$ V), where no charge is passed, to a new potential ($E_1 = -1.10$ V) on the diffusion plateau of the initial electrode process for a given step time τ. A second charge measurement is then made by stepping the potential back from E_1 to E_0 after τ has again elapsed so that the total

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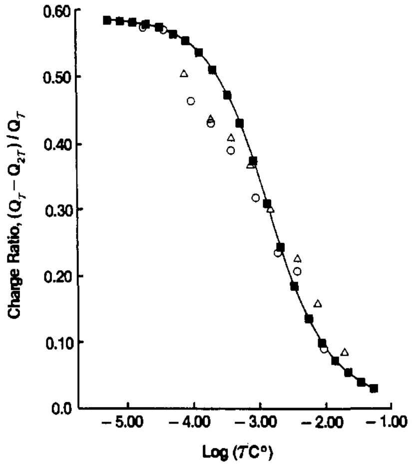

Figure 4. Graphs of experimental charge ratios $(Q_\tau - Q_{2\tau})/Q_\tau$ vs. log (τC^0) for C^0 = 0.2 mM (○), C^0 = 0.4 mM (△), and the theoretical working curve (□). The k_f value for the theoretical curve (solid line) is 1.8×10^3 M^{-1} s^{-1}.

elapsed time is 2τ. The charge ratios, $(Q_\tau - Q_{2\tau})/Q_\tau$, Q_τ being the charge passed at switching time τ and $Q_{2\tau}$ that passed at twice the switching time, are collected for different values of τ. A plot of $(Q_\tau - Q_{2\tau})/Q_\tau$ vs. log (τC^0) is then made. The characteristic shape of this curve (cf. Figure 4) is related to the type of mechanism. By comparison of experimentally determined $(Q_\tau - Q_{2\tau})/Q_\tau$ vs. log (τC^0) curves to theoretical plots,[37] the mechanism and rate constant of the chemical step in the EC process may be determined.

Our experimental data, obtained at low (0.2–0.4 mM) concentrations,[28] exhibit a curve shape consistent with the dimerization mechanism

$$e^- + (phz)PtCl_2(C_2H_4) \rightarrow [(phz)PtCl_2(C_2H_4)]^-\cdot$$

$$[(phz)PtCl_2(C_2H_4)]^-\cdot + (phz)PtCl_2(C_2H_4) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [(phz)PtCl_2(C_2H_4)]_2^-\cdot$$

where k_b is essentially zero; i.e., the equilibrium lies completely to the right. An alternative process that is also consistent with the electrochemical data, coupling of two anion radicals to give dimeric $[(phz)PtCl_2(C_2H_4)]_2^{2-}$, is excluded by the ESR and coulometry experiments described above. Calculation of k_f for the formation of the anion radical dimer $[(phz)PtCl_2(C_2H_4)]_2^-\cdot$ was carried out by visually fitting the experimental data to published theoretical response curves and yields a k_f value of (1.8 ± 0.9) × 10^3 M^{-1} s^{-1}. This value is consistent with our qualitative cyclic voltammetric results.

The details of the structure of $[(phz)PtCl_2(C_2H_4)]_2^-\cdot$ remain to be established. We suggest, however, that dimerization is effected by overlap of the two phenazine rings in a head-to-tail fashion so that interaction between the halves of the dimer involve predominantly π interactions as has been found, for example, in the anion radical dimer of tetracyanoquinodimethan.[41,42] There appears to be some distortion from planarity at all four nitrogen atoms as judged from the magnitudes of the ^{14}N hyperfine splittings, which are approximately related to the spin density ρ_N on sp^2 nitrogen bonded to carbon by[43]

$$A_{^{14}N} = 24\rho_N$$

If there were no distortion with concomitant increase in the p character of the nitrogen-centered orbitals on phenazine, which bear most of the total spin density, then a total ρ of greater than unity would be expected. The observed values for $A_{^{14}N}$ in $[(phz)PtCl_2(C_2H_4)]_2\cdot$ are much larger than that in the phenazine anion radical (5.15 G)[44] and $[(phz)Rh(CO)_2Cl]^-\cdot$ (6.82 G),[1] and as in the rhodium-containing anion radical, there does not appear to be significant spin density on the metal atom. Comparably large ^{14}N splittings in purely organic species, however, are seen in radicals derived from oximes, e.g. *syn*- and *anti*-benzaloximinyl, for which $A_{^{14}N}$ values are 31.6 and 29.2 G, respectively.[45]

Chemical Reduction

Ultraviolet irradiation of chloroform solutions of **5** in the presence of methanol or isopropyl alcohol leads to degradation of the platinum complex and to the formation of the dihydrophenazine cation radical, $H_2(phz)^+\cdot$, identified by its ESR spectrum; this reaction proceeds at a negligible rate in the absence of light. Use instead of CH_3OD as the reducing agent produces $D_2(phz)^+\cdot$, indicating that hydrogen from the –OH (–OD) group in the alcohol is transferred to the phenazine nitrogen atoms. Similar photochemical hydrogen transfer processes, leading to $H_2(phz)^+\cdot$, were observed when benzene solutions of **5** were irradiated in the presence of triethylsilane or tributyltin hydride.

Reduction with Dihydrogen

The reaction between hydrogen and $(phz)PtCl_2(C_2H_4)$ in dichloromethane is catalyzed by platinum black and, less effectively, by palladium black; platinum compounds, such as $[(C_2H_5)_2S]_2PtCl_2$, which form platinum metal in situ, may also be used as catalysts. The reduction product $H[(phz)PtCl_2(C_2H_4)]_2$ (**24**) separates as a dark green, paramagnetic crystalline solid that is, unless the reaction has been carried out for a prolonged period of time, free of metallic platinum. Its electronic spectrum in a Nujol mull exhibits absorption maxima at 248, 310 (sh), 390, 455, 580, 660, and 730 nm. Unexpectedly, **24** is not a platinum hydride. Weak infrared bands at 3190 and 3130 cm^{-1} are due to N–H stretching vibrations. This is confirmed by isotopic labeling, and in $D[(phz)PtCl_2(C_2H_4)]_2$, prepared from **5** and D_2, ν_{N-D} occurs as a medium-intensity band at 2340 cm^{-1}. The labeling is specific since pyrolysis of $D[(phz)PtCl_2(C_2H_4)]_2$ in the mass spectrometer produces ethylene and phenazine containing at most only traces of deuterium. As in the electrochemical reduction, attack occurs at the heterocyclic ring. The XPS spectrum of **24** reveals that the $Pt(4f_{7/2})$ binding energy is 74.0 eV, compared with 73.7 eV in **5**, indicating that platinum is still present in a formal +2 oxidation state. The N(1s) region of the spectrum shows two peaks at 400.3 and 400.8 eV in a 1:1 ratio due to the two chemically nonequivalent nitrogen atoms.

This catalyzed reduction operationally results in transfer of one hydrogen atom to two equivalents of **5**. If it is assumed that each hydrogen atom contributes one spin in the product, then a spin concentration of 6.3 × 10^{20} spins/g should result. Integration of the broad, first-derivative ESR spectrum yields a spin concentration of 6.7 × 10^{20} spins/g, in good agreement with the calculated value.

Oxidation of **24** by *p*-quinone yields dihydroquinone and **5**. The reaction was followed by ^1H NMR spectroscopy and found to proceed quantitatively according to

$$2H[(phz)PtCl_2(C_2H_4)]_2 + C_6H_4O_2 \rightarrow 4(phz)PtCl_2(C_2H_4) + C_6H_4(OH)_2$$

If the oxidation is carried out with a known excess of *p*-quinone, then measurement of the quinone:dihydroquinone ratio at completion, by either ^1H NMR spectroscopy or mass spectroscopy, provides a means of determining the equivalent weight of **24** and,

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(37) Hanafey, M. K.; Scott, R. L.; Ridgeway, T. H.; Reilly, C. N. *Anal. Chem.* **1978**, *50*, 116.

(38) Data taken at higher concentrations, ca. 1.0 mM, show evidence of significant adsorption of the reduced species on the electrode and were not used in the analysis. Double-step chronocoulometry has previously been used to study adsorption of organic species on electrodes.[39,40]

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(42) McPhail, A. T.; Semeniuk, G. M.; Chesnut, D. B. *J. Chem. Soc. A* **1971**, 2174.

(43) Boulton, J. R. In "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Wiley: New York, 1968; p 24.

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(45) Thomas, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 1446.

thereby, the hydrogen content. Application of this technique establishes that the experimental equivalent weight of **24** is 911, compared with a theoretical value of 948, indicating the presence of one readily oxidizable hydrogen/2 equiv of **5**. The structure of $H[(phz)PtCl_2(C_2H_4)]_2$ is, at this time, uncertain. Formally, it is the conjugate acid of the anion radical dimer $[(phz)PtCl_2(C_2H_4)]_2^{-}\cdot$ and presumably it retains the basic structure of that species (vide supra).

Reduction with Silanes

Reduction of $(phz)PtCl_2(C_2H_4)$ occurs with a wide variety of silanes and leads to quite bizarre products. The reactions with R_3SiH (R = Cl, CH_3O, Ph) are complicated and are very solvent dependent. The chemistry in chloroform solutions, in the absence of light, is unusual but does lead to tractable products, and so it has been studied in some detail.

When they are allowed to stand under nitrogen, such solutions of **5** and R_3SiH deposit a deep green, paramagnetic microcrystalline solid whose elemental analysis is consistent with $H_3[(phz)PtCl_2(C_2H_4)]_3PtCl_3$ (**25**). This material is not produced in other solvents such as benzene, ethyl acetate, and carbon tetrachloride. The yields in dichloromethane are very much lower, and an impure bromine analogue is obtained by using bromoform as the solvent. This clearly indicates that the chloroform solvent plays an important part as a halogen source in the reaction. The solubility of **25** in solvents with which it does not react is very low, for which reason large crystals have not been obtained. The poor solubility of this compound makes incisive characterization, particularly of the hydrogen content, difficult and requires reliance on spectroscopic techniques.

A dispersion of **25** in KBr exhibits absorption maxima at 376, 426, 548, 586, 660, 690, and 728 nm, and the electronic spectrum is thus somewhat similar to that of **24** and suggestive of an aggregated structure. The infrared spectrum contains weak N–H stretching bands at 3210 and 3130 cm^{-1} and ν_{Pt-Cl} bands at 330 and 290 cm^{-1}. In the spectrum of the deuterated analogue, prepared with Ph_3SiD as the reducing agent, ν_{N-D} occurs at 2345 cm^{-1}, indicating that the silane is the source of the hydrogen that becomes attached to nitrogen. If a homolytic cleavage of the Si–H bond occurs in the reduction process, then one expects that R_6Si_2 should result as a coproduct. Indeed, when **25** is prepared with use of $(CH_3O)_3SiH$ in chloroform, $(CH_3O)_6Si_2$, indentified by GC–MS analysis, is also formed. The R_3Si portion of the silane is not incorporated into the product since the elemental analyses, X-ray powder patterns, and infrared spectra of the products are independent of the silane employed. Additionally, the X-ray powder pattern is unique and does not contain lines due to **5**, **24**, or platinum metal.

If, as before, it is assumed that, in **25**, each N–H hydrogen atom contributes one spin, then the spin concentration is calculated to be 1×10^{21} spins/g, which compares favorably with the experimental value, obtained by integration of the ESR spectrum, of 1.7×10^{21} spins/g. Oxidation of **25** with a measured amount of *p*-quinone produces $(phz)PtCl_2(C_2H_4)$ and dihydroquinone in a ratio of 1:1.5. From this, an equivalent weight of 555 is obtained, in good agreement with a value of 575 calculated on the assumption that all three N–H hydrogens are removed in the oxidation and that the $(phz)PtCl_2(C_2H_4)$ units are not irreversibly modified upon formation of the silane reduction product.

The structure of $H_3[(phz)PtCl_2(C_2H_4)]_3PtCl_3$ is not at all apparent, and this issue is unlikely to be resolved until some means of preparing crystals suitable for X-ray analysis is discovered. We note, however, that the compositional formula implies the presence of two kinds of chemically nonequivalent platinum in a 1:3 ratio. Indeed, the deconvoluted XPS spectrum, obtained after argon ion sputtering to clean the surface, demonstrates two characteristic Pt($4f_{5/2,7/2}$) doublets in a ratio of 1:2.7 whose binding energies are 73.7, 77.0 and 72.2, 75.6 eV, respectively (cf. Figure 5).

Hydrosilation Catalysis

Addition of silanes to olefins is efficiently catalyzed by $(phz)PtCl_2(C_2H_4)$.[3] Since **5** readily forms free radical species in the presence of silanes, it is of interest to determine whether the catalytic hydrosilation reaction involves silicon-centered radicals or if it proceeds by the Chalk–Harrod mechanism in which Pt(II) and Pt(IV) act as reaction templates.[46] Mechanistic information is available from the product distribution in the addition of trichlorosilane to 1-methylcyclohexene. Selin and West[47] found that *cis*-1-methyl-2-(trichlorosilyl)cyclohexane was the principal product when hydrosilation was initiated by ultraviolet light or peroxides and presumably proceeded by a free radical mechanism. Use of chloroplatinic acid, on the other hand, led to (cyclohexylmethyl)trichlorosilane, and uncatalyzed thermal additions produced *cis*- and *trans*-1-CH_3-2-$Cl_3SiC_6H_{10}$ as well as $C_6H_{11}CH_2SiCl_3$. In refluxing dichloromethane, the reaction of trichlorosilane with 1-methylcyclohexene in the presence of a catalytic amount of $(phz)PtCl_2(C_2H_4)$ produces (cyclohexylmethyl)trichlorosilane; other isomers, if present, were below the detection limits of ^1H NMR spectroscopy. The structure of this isomer is established by off-resonance decoupled and low-power noise-decoupled ^{13}C NMR spectra (cf. Experimental Section). Thus, it appears that the hydrosilation reaction occurs by equilbrium displacement of ethylene in **5** by 1-methylcyclohexene (an analogous reaction was demonstrated earlier with styrene) followed, as in the case of conventional catalysts, by oxidative addition of $HSiCl_3$.

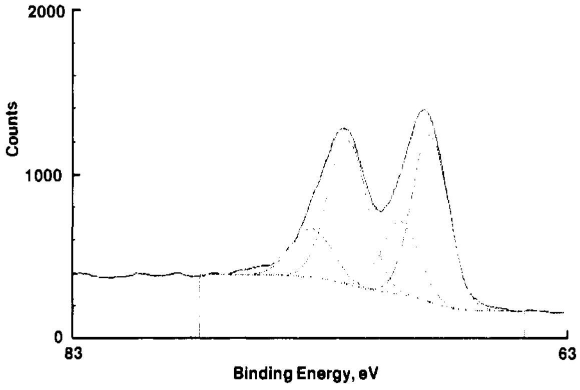

Figure 5. XPS spectrum (Pt(4f) region) for **25**.

Experimental Section

Infrared, NMR, ESR, XPS, and TPD spectra were obtained by methods described in ref 1.

Electrochemical measurements were made at 20 ± 2 °C. A three-electrode configuration was used, employing a glassy-carbon working electrode, a platinum spiral auxiliary electrode, and a AgCl/Ag (1.0 M KCl saturated with AgCl) reference electrode. The reference electrode was connected to the working electrode compartment via a salt bridge terminating in a modified Luggin capillary. The working solution was 0.1 M in $(n\text{-}C_4H_9)_4NPF_6$ (Southwestern Analytical Chemicals Inc., electronic grade, used as received). Methylene chloride was used as supplied by Burdick and Jackson. All potentials reported are uncorrected for the junction potential; however, ferrocene was used as an internal reference system for which $E°'(Cp_2Fe^+/Cp_2Fe) = +0.48$ V.[48]

iR-drop problems were minimal, and so no compensation was used. Working solutions were deoxygenated with purified argon or nitrogen presaturated with solvent. Solvent and supporting electrolyte stock solutions were dried over activity 1 80–200 mesh alumina (Fisher Scientific Co.) before use.

Cyclic voltammograms of **5** were recorded with a Princeton Applied Research Model 170 electrochemistry system. Double-step chronocoulometry transients were recorded with a system consisting of a PAR Model 175 universal programmer, a Model 173 potentiostat/galvanostat, a Model 179 digital coulometer, a Biomation Model 805 waveform recorder, and a Heath Model SR204 strip chart recorder. Charge transients stored in the Biomation waveform recorder were displayed on an oscilloscope before output to the strip chart recorder.

$(phz)PtCl_2(C_2H_4)$ (5). Phenazine (0.60 g, 3.3 mmol, obtained from Aldrich Chemical Co.) in 20 mL of hot acetonitrile was added to a solution of 1.28 g (3.3 mmol) of $KPtCl_3(C_2H_4)$ in 20 mL of the same solvent. After the mixture was allowed to stand for 24 h, the solids that

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separated were recrystallized from dichloromethane/ethanol to give 0.58 g of product as yellow needles. The original mother liquor was evaporated and the residue similarly recrystallized to give 0.32 g of additional product. The total yield was 0.90 g (59%). X-ray powder pattern [*d*, Å (I/I_0)]: 8.37 (40), 6.97 (100), 6.62 (70), 6.11 (60), 4.90 (40), 4.58 (70), 4.38 (20), 4.28 (20), 4.10 (75), 3.78 (50), 3.72 (25), 3.04 (60), 2.30 (15). The analogous phenazine *N*-oxide, pyrazine, quinoxaline, dimethylpyrazine, tetramethylpyrazine, and acridine compounds were prepared in a similar manner.

(phz)PtCl$_2$(Ph$_3$P) (14) and (phz)[PtCl$_2$PPh$_3$]$_2$ (18). Triphenylphosphine (0.13 g, 0.5 mmol) and 0.24 g (0.5 mmol) of (phz)PtCl$_2$(C$_2$H$_4$) in 10 mL of acetonitrile were refluxed and stirred overnight. Filtration of the cooled solution afforded 0.10 g of bright orange **18**. The filtrate was concentrated and cooled. The yellow product that separated was recrystallized from acetonitrile to yield 0.18 g of **14** as yellow plates, $\delta(^{31}P)$ 2.6 (J_{Pt-P} = 3762 Hz, 85% H_3PO_4 reference, $CDCl_3$ solvent).

(phz)PtCl$_2$[S(C$_2$H$_5$)$_2$] (16). A mixture of 0.35 g of **5**, 0.2 mL of diethyl sulfide, and 25 mL of benzene was refluxed overnight. The residue remaining after evaporation of the solvent was extracted with 40 mL of boiling hexane. Evaporation of this extract left 0.1 g of $PtCl_2[S(C_2H_5)_2]_2$, identified by infrared analysis. The hexane-insoluble material was recrystallized from toluene/heptane to give 0.12 g of **16** as yellow-orange microcrystals.

(phz)PtCl$_2$(C$_2$H$_4$)·AgCF$_3$SO$_3$ (20). A solution of 0.25 g of silver trifluoromethanesulfonate in 6 mL of benzene was added to 0.47 g (1 mmol) of **5** in 30 mL of hot benzene. After 15 min, the yellow product was collected on a filter, washed with fresh solvent, and vacuum-dried. The yield was 0.57 g.

(phz)PtCl$_2$(C$_2$H$_4$)·HCl (21). A stream of anhydrous hydrogen chloride was passed through a dichloromethane solution of 0.5 g of **5**. The reaction mixture was filtered and the filtrate saved. The solid phase was recrystallzed by slow rotary evaporation of a ethanol/dichloromethane solution to give 0.10 g of product. The filtrate was diluted with heptane and concentrated to give solids that were similarly recrystallized to give 0.15 g of additional **21**. Infrared spectra and elemental analyses for the two crops were the same.

(phz)$_2$(PtCl$_2$)$_2$(C$_2$H$_4$) (22). A suspension of 0.4 g of **5** in 10 mL of deoxygenated toluene was heated under nitrogen with stirring at 110 °C (oil bath) for 16 h. After it was cooled to room temperature, the solid product was collected on a filter, washed with toluene and then dichloromethane, and vacuum dried. The yield of powdery, maroon **22** was 0.29 g.

PPN$^+$[(phz)PtCl$_3$]$^-$ (23). A solution of 0.64 mmol of **5** and 0.64 mmol of $PPN^+PtCl_3(C_2H_4)^-$ in 50 mL of chloroform was refluxed and stirred for 16 h. The solvent was removed under reduced pressure and the residue then extracted with dichloromethane and with acetone. The combined extracts were chromatographed on a 8 × 0.75 in. silica gel column. Acetone/CH_2Cl_2 (1:10) eluted a small amount of unidentified yellow material. The purple product was eluted with 1:4 acetone/CH_2Cl_2 and recrystallized from dichloromethane/butanone. The yield was 0.28 g.

Electrochemical Reduction of (phz)PtCl$_2$(C$_2$H$_4$). Preparative electrochemical experiments were carried out with a PAR Model 175 function generator, a PAR Model 379 coulometer, and a Wenking Model ST-72 potentiostat. A water-jacketed cell maintained at 4 °C held the sample, which was dissolved in 0.1 M solution of $(n\text{-}C_4H_9)_4NBF_4$ in dichloromethane. Nitrogen presaturated with solvent was used to deoxygenate this solution. The reference electrode was saturated aqueous calomel. The working electrode was constructed of platinum gauze.

Reduction of (phz)PtCl$_2$(C$_2$H$_4$) was carried out at a potential of −0.9 V until the current had declined to 4% of the intial value, at which point, 0.49 faraday/mol of platinum had been passed. Aliquots of the deep blue-green solution was transferred under nitrogen to ESR tubes or a rectangular cuvette for electronic spectroscopy. The samples were degassed by three freeze–pump–thaw cycles and then sealed under vacuum with a torch.

Reduction with Sodium. With use of a vacuum line, 5 mL of acetonitrile (dried over 5A molecular sieves and then degassed) was condensed onto 0.047 g of **5** and 0.26 g of 0.4% sodium amalgam. After it was shaken for about 5 min, the blue-green solution was filtered through a coarse frit into an ESR tube. The tube was cooled to −178 °C and sealed off under vacuum. Similar reductions were performed with sodium amalgam in 1,2-dimethoxyethane or with sodium naphthalide in tetrahydrofuran to give $[(phz)PtCl_2(C_2H_4)]_2^-{\cdot}Na^+$, whose ESR and optical spectra matched those of the radical prepared by electrochemical means. If the chemical reductions are carried out for a prolonged period, the blue-green color is replaced by the red of the phenazine anion radical and a platinum mirror forms on the walls of the reaction vessel.

H[(phz)PtCl$_2$(C$_2$H$_4$)]$_2$ (24). A solution of 0.40 g of **5** in 20 mL of dichloromethane was prepared under nitrogen. A small amount of platinum black was added, and hydrogen was passed over the stirred solution for 3.5 h. The reaction vessel was then flushed with nitrogen and opened in air. (*Caution*! Air should not be admitted when the system still contains hydrogen.) Filtration afforded 0.26 g of **24** as a dark green solid, which was dried by pumping and stored under vacuum. X-ray powder pattern [*d*, Å (I/I_0)]: 7.22 (65), 6.74 (100), 6.28 (85), 6.01 (70), 4.86 (80), 4.56 (85), 2.74 (55). D[(phz)PtCl$_2$(C$_2$H$_4$)]$_2$ was prepared in a similar manner with D_2 instead of hydrogen.

Oxidation of H[(phz)PtCl$_2$(C$_2$H$_4$)]$_2$. A mixture of 0.18 g of **24**, 0.041 g of resublimed *p*-quinone, and 35 mL of dichloromethane was stirred overnight under nitrogen. After filtration to remove a trace of black solids, solvent was removed and the residue taken up in $CDCl_3$ for analysis by ^1H NMR spectroscopy. Integration of the peaks at 6.80, 6.73, and 5.27 ppm, due, respectively, to *p*-quinone, dihydroquinone, and the ethylene protons in **5** was used to establish the stoichiometry of the oxidation (vide supra). The quinone and hydroquinone peaks were identified by addition of increments of the pure compounds. The quinone:hydroquinone ratio was found to be 2.8:1 by NMR analysis and 2.9:1 by direct-inlet mass spectroscopy.

Reaction of (phz)PtCl$_2$(C$_2$H$_4$) with Triphenylsilane. A mixture of 0.47 g of **5**, 0.27 g of Ph_3SiH, and 25 mL of chloroform (freshly distilled from $CaSO_4$) was stirred under nitrogen for 15 min and then left undisturbed for 3 h. The fine, deep green microcrystalline product was collected on a frit, washed with fresh solvent, and vacuum dried. The yield of **25** was 0.23 g. The compound is stored under nitrogen. X-ray powder pattern [*d*, Å (I/I_0)]: 9.28 (40), 8.12 (35), 6.11 (100), 5.10 (40), 4.09 (80), 3.17 (40). A similar reaction using Ph_3SiD afforded the N-deuterated analogue of **25**, which had an identical X-ray powder pattern and microanalysis. Oxidation of **25** was carried out with *p*-quinone as described above.

Other silanes were screened to determine if they exhibited similar reducing behavior. Active were 1,1,2-trimethyldisilane, 1,1,1-trimethyldisilane, diethoxysilane, phenylsilane, diethylsilane, octylsilane, pentamethyldisiloxane, diphenylsilane, trichlorosilane, and trimethoxysilane.

Catalysis of Hydrosilation. A mixture of 20 mL of trichlorosilane, 25 mL of chloroform, 8.1 g of 1-methylcyclohexene, and 0.055 g of **5** was stirred and refluxed under nitrogen for 6 days. Distillation of the reaction mixture through a spinning head column afforded 2.0 g of $C_6H_{11}CH_2SiCl_3$. Mass spectrum [*m*/*e* (assignment)]: 83 ($C_6H_{11}^+$), 133 ($SiCl_3^+$), 197 ($M^+ - C_2H_4$), 299 (M^+). Exact mass: calcd for $^{12}C_7{}^1H_{13}{}^{35}Cl_2{}^{28}Si$, 229.9852; found, 229.985 (5). IR (film): 1391, 2850, 2925, 1449, 570 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 33.15 (CH), 32.58 (CH_2Si), 35.42 ($C_{2,6}$) 25.94 ($C_{3,5}$), 25.60 (C_4).

Registry No. **1**, 92-82-0; **2**, 91-19-0; **3**, 290-37-9; **4**, 304-81-4; **5**, 78713-13-0; **6**, 95662-18-3; **7**, 78713-20-9; **8**, 96039-56-4; **9**, 95662-23-0; **10**, 95662-22-9; **11**, 81273-55-4; **13**, 96148-93-5; **14**, 96094-23-4; **15**, 96094-24-5; **16**, 96039-57-5; **17**, 96039-58-6; **18**, 96039-59-7; **19**, 96039-60-0; **20**, 96039-61-1; **21**, 84709-16-0; **22**, 96039-62-2; **23**, 96039-64-4; (py)PtCl$_2$(C$_2$H$_4$), 12078-66-9; (acd)PtCl$_2$(C$_2$H$_4$), 95662-17-2; (pyr)PtCl$_2$(CO), 96094-25-6; (quinox)PtCl$_2$(CO), 96094-26-7; (phz)PtCl$_2$(CO), 96094-27-8; (phz *N*-ox)PtCl$_2$(CO), 96094-28-9; (2,6-Me$_2$pyr)PtCl$_2$(CO), 96094-29-0; (2,3,5,6-Me$_4$pyr)PtCl$_2$(CO), 96094-30-3; (acd)PtCl$_2$(CO), 96039-65-5; (py)PtCl$_2$(CO), 51261-84-8; $(P_4As)_2PtCl_4$, 62873-94-3; $(Ph_3P)_2PtCl_2$, 10199-34-5; $[(C_7H_7)_3P]_2Pt_2Cl_4$, 42958-17-8; [((*o*-tol)O)$_3$P]$_2$PtCl$_2$, 41871-77-6; $PtCl_2[S(C_2H_5)_2]_2$, 14873-92-8; $KPtCl_3(C_2H_4)$, 12012-50-9; $PPN^+PtCl_3(C_2H_4)^-$, 96039-66-6; $(n\text{-}C_4H_9)_4NPtCl_3(C_2H_4)$, 34778-37-5; $H_2(phz)^{+\cdot}$, 35862-61-4; $phz^{-\cdot}Na^+$, 79845-29-7; $phz^{-\cdot}$, 34467-89-5; $D_2(phz)^{+\cdot}$, 96021-78-2; 2,6-Me$_2$pyr, 108-50-9; 2,3,5,6-Me$_4$pyr, 1124-11-4; acd, 260-94-6; $C_6H_{11}CH_2SiCl_3$, 18388-16-4; Ph_3SiH, 789-25-3; Ph_3SiD, 18536-60-2; Cl_3SiH, 10025-78-2; $(CH_3O)_3SiH$, 2487-90-3; $(C_2H_5)_3SiH$, 617-86-7; $(CH_3O)_6Si_2$, 5851-07-0; $(n\text{-}C_4H_9)_3SnH$, 688-73-3; dihydroquinone, 123-31-9; 1,1,2-trimethyldisilane, 814-74-4; 1,1,1-trimethyldisilane, 18365-32-7; diethoxysilane, 18165-68-9; phenylsilane, 694-53-1; diethylsilane, 542-91-6; octylsilane, 871-92-1; pentamethyldisiloxane, 1438-82-0; diphenylsilane, 775-12-2; 1-methylcyclohexene, 591-49-1; *p*-quinone, 106-51-4.

Supplementary Material Available: Table S1, giving analytical data (2 pages). Ordering information is given on any current masthead page.