

RHODIUM(I) AND IRIIDIUM(I) COMPLEXES OF PHENAZINE AND RELATED LIGANDS

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(Received October 12th, 1982)

Summary

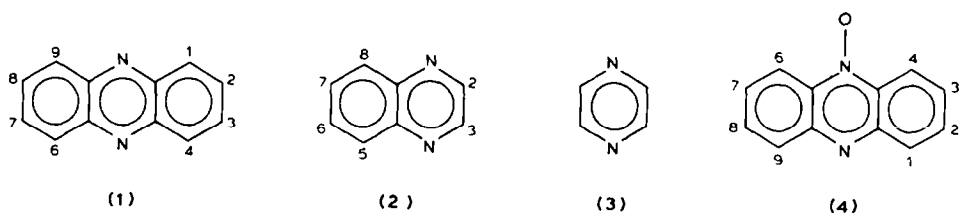
Bridge cleavage of $[MCl(C_8H_{12})]_2$ and $[MCl(CO)_2]_2$ ($M = Rh, Ir$) with the ligands phenazine, phenazine-*N*-oxide, quinoxaline and pyrazine affords (ligand) $MCl(C_8H_{12})$ and (ligand) $MCl(CO)_2$. The bimetallic compounds (phenazine) $[Rh(CO)_2Cl]_2$ and (pyrazine) $[Rh(CO)_2]_2$ were also prepared. The pyrazine complex reacts with iodine to form (pyrazine) $[Rh(CO)_2]_2I_{4.2}$. (Phenazine) $Rh(CO)_2Cl$ was electrochemically reduced to the anion radical whose EPR spectrum is reported. Chloroplatinic acid and (phenazine) $Rh(CO)_2Cl$ react in methanol at room temperature to form (phenazinium) $_2PtCl_6$ and at reflux to provide (dihydrophenazine) $_2PtCl_2$.

Introduction

Previously, we reported the synthesis of palladium(II) and platinum(II) complexes of phenoselenazine and phenothiazine and the conversion of these materials to partially oxidized cation radical salts by treatment with iodine [1]. Phenazine (PNZ) is also an electroactive ligand and it readily forms both the anion radical and the dihydrophenazine cation radical [2]. We have extended our earlier work to include a study of the coordination complexes of phenazine and related heterocycles and those containing rhodium(I) and iridium(I) are the subject of this paper.

Results and discussion

The ligands employed in this work are phenazine (1), quinoxaline (2), pyrazine (3), and phenazine-*N*-oxide (4). Halogen bridged rhodium(I) or iridium(I) dimers are readily cleaved by 1-4 in organic solvents such as acetonitrile, benzene, or methylene chloride. For example, (PNZ) $RhCl(COD)$ (5) ($COD = 1,5$ -cyclooctadiene) is obtained in 75% yield from the reaction of 1 with $[RhCl(COD)]_2$. On recrystallization of 5 from acetonitrile, needle crystals of the α form separate but, on standing,



the mother liquor deposits plate-like crystals of the β -form. The elemental analyses and infrared spectra, cf. Tables 1–4, of these two compounds are the same but the X-ray powder diffraction patterns of each are distinct, indicating that crystal polymorphs have been obtained. (Phenazine)IrCl(COD) (6) obtained from 1 and [IrCl(COD)]₂, is isomorphous with α -(PNZ)RhCl(COD). Polymorphism was not observed in (PNZ)RhBr(COD) (7), or (phenazine oxide)RhCl(COD) (8).

TABLE I
ANALYSIS DATA

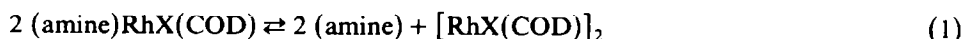
| Compound | Analysis (Calcd.(%) (found)) | | | | |
|---|------------------------------|--------------|--------------|----------------|----------------------------------|
| | C | H | N | Cl | Mol.wt. |
| α -(Phenazine)RhCl(COD) (5a) | 56.3 (56.2) | 4.7 (4.7) | 6.6 (6.6) | 8.2 (8.5) | 426 (318, CHCl ₃) |
| β -(Phenazine)RhCl(COD) (5b) | (56.2) | (4.7) | (6.6) | | |
| (Phenazine)IrCl(COD) (6) | 46.6 (46.5) | 3.9 (3.7) | 5.4 (5.6) | | 515 (322) |
| (Phenazine)RhBr(COD) (7) | 51.0 (49.5) | 4.2 (4.2) | 5.9 (5.6) | | 471 (360) |
| (Phenazine oxide)RhCl(COD) (8) | 54.3 (54.1) | 4.5 (4.7) | 6.3 (6.4) | | |
| (Quinoxaline)RhCl(COD) (9) | 51.1 (50.6) | 4.8 (4.9) | 7.5 (7.7) | | |
| (Pyrazine)[RhCl(COD)] ₂ (10) | 41.9 (42.0) | 4.9 (5.1) | 4.9 (5.1) | 10.7 (10.5) | |
| (Phenazine)RhCl(CO) ₂ (11) | 44.9 (44.6) | 2.1 (2.0) | 7.5 (7.2) | 9.4 (9.3) | 374 (370) |
| (Phenazine oxide)RhCl(CO) ₂ (12) | 43.0 (44.0) | 2.1 (2.1) | 7.2 (7.5) | | |
| (Phenazine)IrCl(CO) ₂ (13) | 36.3 (36.3) | 1.7 (1.4) | 6.1 (6.1) | | |
| (Phenazine)[RhCl(CO) ₂] (14) | 33.7 (34.0) | 1.4 (1.2) | 4.9 (5.0) | | |
| (Pyrazine)[RhCl(CO) ₂] (15) | 20.5 (20.4) | 0.8 (0.6) | 6.0 (6.0) | | |
| (Pyrazine)[RhCl(CO) ₂] ₄ (16) ^a | 9.6 (9.2) | 0.4 (0.5) | 3.0 (3.1) | 7.1 7.0 | |
| (Phenazinium) ₂ PtCl ₆ (18) | 37.4 (36.8) | 2.3 (2.3) | 7.3 (6.9) | 27.7 (28.0) | |
| (Dihydrophenazine) ₂ PtCl ₂ (19) ^b | 41.1 (41.1) | 2.9 (2.4) | 8.0 (8.1) | 20.3 (20.4) | |

^a I, 53.2 (53.3). ^b Pt, 27.8 (27.6); Rh, 0.0 (< 0.3).

TABLE 2
INFRARED SPECTRAL DATA

| Compound | ν_{\max} (cm ⁻¹) (Nujol mull) (± 5 cm ⁻¹) |
|----------|---|
| 5a | 1605(w), 1520(s), 1470(m), 1430(m), 1410(w), 1380(m), 1370(m), 1215(m), 1120(w), 995(w), 965(s), 875(m), 830(s), 775(m), 760(vs), 625(m), 600(m), 455(w), 270(s) |
| 6 | 1600(w), 1560(w), 1520(s), 1470(m), 1430(s), 1215(m), 1115(w), 1010(m), 985(m), 910(w), 830(m), 765(vs), 620(m), 600(w), 390(w), 290(s) |
| 7 | 1600(w), 1515(s), 1470(s), 1430(s), 1410(w), 1380(m), 1365(m), 1215(m), 1115(w), 1005(w), 995(w), 965(s), 870(m), 830(s), 760(vs), 620(m), 595(m), 450(w) |
| 8 | 3100(w), 1600(w), 1580(s), 1540(m), 1520(m), 1505(s), 1475(s), 1425(s), 1410(s), 1360(m), 1265(s), 1125(s), 1020(m), 995(m), 965(s), 860(w), 830(w), 780(s), 765(vs), 650(w), 640(vs), 620(s), 595(m), 560(m), 450(m), 405(m), 380(m), 270(s) |
| 9 | 1580(w), 1500(s), 1480(m), 1520(w), 1365(s), 1340(w), 1215(m), 1230(m), 1130(s), 1040(s), 1000(m), 955(s), 875(s), 860(s), 765(s), 630(m), 420(m), 410(w), 270(s) |
| 10 | 1465(w), 1430(w), 1420(s), 1395(s), 1380(w), 1330(w), 1305(w), 1220(w), 1170(s), 1105(m), 1000(s), 965(s), 870(m), 815(s), 485(m), 460(m), 330(m), 280(s) |
| 11 | 2090(vs), 2040(vs), 2015(vs), 1970(s), 1605(w), 1520(s), 1470(s), 1435(s), 1375(s), 1355(m), 1225(m), 1150(w), 1120(s), 1005(w), 835(s), 760(s), 750(s), 610(m), 590(s), 530(m), 480(m), 470(m), 395(w), 320(s), $\nu(\text{CO})(\text{CHCl}_3)$: 2092, 2024 |
| 12 | 2080(vs), 2020(vs), 2000(vs), 1580(s), 1535(w), 1510(m), 1480(s), 1430(s), 1410(s), 1270(s), 1125(s), 780(s), 760(s), 655(m), 640(s), 600(m), 310(m), $\nu(\text{CO})(\text{CHCl}_3)$: 2093, 2021 |
| 13 | 2070(vs), 1990(s), 1960(vs), 1605(w), 1520(s), 1475(w), 1435(s), 1370(w), 1355(w), 1145(w), 1120(m), 830(m), 750(s), 595(m), 330(w), $\nu(\text{CO})(\text{CHCl}_3)$: 2181, 2002 |
| 14 | 2105(vs), 2085(vs), 2010(vs), 1970(sh), 1620(w), 1525(s), 1470(m), 1435(m), 1430(s), 1360(m), 1225(m), 1130(s), 840(m), 760(s), 605(m), 590(s), 565(m), 475(s), 310(s), 290(m), $\nu(\text{CO})(\text{CHCl}_3)$: 2092, 2024 |
| 15 | 3110(w), 2110(m), 2020(s), 1985(m), 1425(s), 1160(m), 1125(m), 810(s), 510(w), 490(m), 460(w), 435(w), 300(m) |
| 16 | 3110(w), 2105(s), 2015(s), 1425(s), 1160(m), 1120(m), 805(s), 605(w), 505(m), 490(m), 470(m), 300(m) |
| 18 | 3460(br,s), 1640(m), 1615(m), 1520(s), 1470(m), 1415(m), 1360(m), 1130(s), 935(w), 825(s), 770(m), 750(s), 730(s), 605(s), 590(m), 325(s) |
| 19 | 2900(br), 1620(m), 1520(m), 1355(m), 1330(w), 1240(m), 1230(m), 1135(m), 825(s), 740(s), 605(s), 590(s), 455(m), 310(s) |

The ¹H NMR spectra of the (phenazine)(cyclooctadiene)rhodium(I) compounds reveal deshielded peri-protons at ca. 10.2 ppm, cf. Table 3. The deshielding is due to the diamagnetic interaction with the Rh 4d_{z²} electrons. These protons appear as a doublet due to the 8 Hz coupling with the adjacent H(3,7) protons. Interaction with the larger, more diffuse 5d_{z²} electrons appears to be less efficient and the peri-protons in (PNZ)IrCl(COD) have δ 9.85 ppm. In chloroform solution, there is a slow (on the NMR time scale) dissociation, eq. 1. The proton NMR spectra of **5** and **7** show peaks due to [RhX(COD)]₂ at 4.24 ppm (X = Cl) and 4.45 ppm (X = Br) which disappear when excess phenazine is added. The equilibrium constants, given by eq. 2, were obtained by ¹H NMR spectroscopy. The concentration of the



$$K_{\text{c4}} = \frac{[\text{amine}]^2 \{[\text{RhX}(\text{COD})]_2\}}{[(\text{amine})\text{RhX}(\text{COD})]^2} \quad (2)$$

TABLE 3
NUCLEAR MAGNETIC RESONANCE DATA

| Compound | δ |
|----------|---|
| 5a | ^1H : 10.25(d,8,H(1)); 8.3–7.9(m); 5.06(s, =CH); 3.44(s, =CH); 2.65(m,CH ₂); 1.9(m,CH ₂) |
| 6 | ^1H : 9.85(d,9,H(1)); 8.5–7.7(m); 4.8(s, =CH); 3.05(s, =CH); 2.45(m,CH ₂); 2–1.5(m,CH ₂) |
| 7 | ^1H : 10.2(d,8,H(1)); 8.4–7.8(m); 5.15(s, =CH); 3.48(s, =CH); 2.65(m,CH ₂); 1.9(m,CH ₂) |
| 8 | ^1H : 10.2(d,8,H(1)); 8.7–7.8(m); 5.04(s, =CH); 3.48(s, =CH); 2.5(m,CH ₂); 1.8(m,CH ₂) |
| 9 | ^1H : 8.96(s,H(2)); 8.7(brs,H(5)); 7.92(s,H(6)); 4.25(s, =CH); 2.55(m,CH ₂); 1.9(m,CH ₂) |
| 10 | ^1H : 8.69(s); 4.24(s, =CH); 2.55(m,CH ₂); 1.9(m,CH ₂) |
| 11 | ^1H : 9.39(d,8,H(1)); 8.39(d,8,H(4)); 8.10(t,8,H(2)); 7.97(t,8,H(3)); ^{13}C : 128.2(C(1)); 130.1(C(4)); 131.0(C(3)); 133.1(C(2)); 141.9(C(10a)); 144.4(C(4a)); 179.5(d,72,CO); 182.7(d,70,CO) |
| 12 | ^1H : 9.33(d,8,H(1)); 8.69(d,8,H(4)); 8.04(t,8,H(2)); 7.83(t,8,H(3)) ^{13}C : 119.3(C(4)); 129.8(C(1)); 130.5(C(3)); 133.4(C(2)); 136.9(C(10a)); 144.4(C(4)) 179.5(d,71,CO); 182.6(d,69,CO) |
| 13 | ^1H : 9.56(dd,9,1,1,7,H(1)); 8.43(dd,8,9,1,7,H(4)); 8.12(ddd,1,7,6,9,8,6,H(2)); 7.99(ddd,1,5,6,9,8,6,H(3)) (at 200 MHz) |
| 14 | ^1H : 9.43(bd,H(1),H(4)); 8.12(bd,H(2),H(3)); ^{13}C : 129.9(C(1,4)); 133.8(C(2,3)); 144.0(C(4a,10a)); 181.3(CO) |

rhodium complex was established by integration of the 10.2 ppm peak and that of [RhX(COD)]₂ by integration of the 4.24 or 4.45 ppm peaks; the concentration of the free amine was assumed to be twice that of the rhodium dimer. K_{eq} values of 0.42, 0.24 and 15.2 were obtained for **5**, **7** and **8** respectively. The phenazine-*N*-oxide complex is significantly more dissociated than either of the phenazine complexes. This may be due to the electron-withdrawing effect of the *N*-oxide moiety, polarized

TABLE 4
ELECTRONIC SPECTRAL DATA

| Compound | λ_{max} (log ϵ)(nm) |
|----------|---|
| 5 | 250(4.67), 350(sh), 360(4.01), [CHCl ₃]; 242, 265(sh), 360, 375, 445 [Nujol] |
| 6 | 250(4.98), 350(sh), 360(4.25) [CHCl ₃] |
| 7 | 248(4.39), 350(sh,3.53), 360(3.61) [CHCl ₃] |
| 8 | 268(4.59), 347(sh), 362(3.97), 380(3.88), 395(3.78), 422(3.60) [CHCl ₃]; 265, 280(sh), 350, 445 [Nujol] |
| 9 | 232, 296, 388 [Nujol] |
| 10 | 260(4.18), 305(3.62), 349(3.60) [CHCl ₃]; 232, 260(sh), 360, 393 [Nujol] |
| 11 | 254(5.02), 335(4.11), 355(sh), 364(4.22), 375(4.27), 4.20(sh) [CHCl ₃] |
| 12 | 264(4.93), (3.89), 370(s), 378(4.00), 396(3.84), 418(3.93) [CHCl ₃] |
| 13 | 254(4.94), 356(4.07), 376(4.16), 380(sh), 420(sh) |
| 14 | 254(5.02), 335(4.11), 355(sh), 364(4.22), 375(4.27), 420(sh) [CHCl ₃] |

N^+-O^- , which reduces the electron density on the opposite nitrogen atom and weakens the Rh–N bond. The greater stability of the rhodium bromide complex **7** may be associated with the increased Rh–halogen distance on going from Cl to Br, thus reducing nonbonded repulsive interactions between the halogen atom and the phenazine peri-hydrogen atoms. Steric effects can account for other trends observed in relative stabilities. The 1H NMR spectrum of (PNZ)IrCl(COD) shows no peaks due to $[IrCl(COD)]_2$ and so **6** is not detectably dissociated by NMR criteria, indicating that the Ir–ligand bond strength (or stability) is greater than in the Rh counterpart.

(Quinoxaline)RhCl(COD) (**9**) appears from NMR experiments to be completely dissociated. This process, however, is rapid and the averaging of the peri-H(5) environments leads to a broad resonance since the chemical shift difference between H(5) in the free and complexed ligand is large because of the deshielding effect of the metal in the complex. The same rapid exchange of rhodium between the two nitrogen sites in quinoxaline and $[RhCl(COD)]_2$ also averages the chemical shifts of H(2,3) and H(6,7) but since $|\delta(\text{free})-\delta(\text{bound})|$ is much smaller for these protons, sharp resonances are observed.

Pyrazine, which has no peri-hydrogen atoms at all and thus no strong repulsive interactions with organometallic groups bonded to the ring nitrogen atom, forms the bimetallic rhodium compound (pyrazine) $[RhCl(COD)]_2$ (**10**) regardless of the ratio of starting materials employed. This compound, and also (pyridine)RhCl(COD), are completely dissociated in chloroform which suggests inherent weakness of the Rh–N bond. The stability of the bimetallic pyrazine compound **10** may be associated in part with its crystal lattice energy. For the reverse of reaction 1, Pribula and Drago [3] have reported ΔH to be $-12.5 \text{ kcal mol}^{-1}$ when the amine donor molecule is pyridine. Although, as judged by pK_b values (5.25 for pyridine, ca. 13 for phenazine), phenazine is a much weaker base than pyridine, the NMR data show that phenazine forms a stronger Rh–N bond. Failure of pK_b data to predict relative stabilities in the absence of strong π back-bonding in these compounds is due to the intervention of what we term the orthogonality effect. Molecular models indicate that nonbonded repulsions between the phenazine peri-hydrogen atoms and the chlorine and cyclooctadiene groups in **5** cause the heterocyclic ligand to twist so that its molecular plane is perpendicular to the rhodium coordination plane [4]. In this geometry, the phenazine π^* and trans-olefin π^* orbitals do not overlap with and compete for

TABLE 5
THERMAL PROGRAMMED DESORPTION DATA

| Compound | $T(^{\circ}C)$ for onset of evolution of heterocyclic amine | 1,5-Cyclooctadiene |
|---|---|--------------------|
| 5 | 120 | 240 |
| 6 | 125 | 130 |
| 8 | 170 | 170 |
| 9 | 80 | 220 |
| 10 | 170, 280 ^a | 220 |
| (pyridine)RhCl(C ₈ H ₁₂) | 70, 260 ^a | |

^a Bimodal distribution.

electron density from the same, filled Rh 4*d* orbital. This sterically enforced twisting of the phenazine ligand leads to unexpectedly strong rhodium–nitrogen bonds.

Thermal stability of the cyclooctadiene derivatives was qualitatively assessed by thermally programmed mass spectroscopic data, Table 5. In these experiments, the ion currents due to cyclooctadiene and the nitrogen-containing ligand are followed as a function of sample temperature and the temperature for onset of ligand loss is noted. For both metal–nitrogen and metal–olefin bond strengths, the trends observed are phenazine > quinoxaline > pyridine and Rh < Ir.

Halogen bridge cleavage reactions were also used to prepare (phenazine)RhCl(CO)₂ (**11**) and (phenazine-*N*-oxide)RhCl(CO)₂ (**12**). The iridium(I) analogue, (phenazine)IrCl(CO)₂ (**13**), was obtained in low yield from phenazine and polymeric, metal–metal bonded [IrCl(CO)₃]_x.

These metal carbonyl complexes exhibit greater solubility in acetonitrile and in aromatic and chlorinated hydrocarbons than do the corresponding cyclooctadiene compounds. In chloroform, they do not dissociate with cleavage of the metal–nitrogen bond. This is readily established by integration of the ¹H NMR spectra which show the expected ratio of the low field peri-protons to other aromatic protons, and by FTIR spectra of chloroform solutions which reveal the absence of the characteristic 2106 cm⁻¹ band of [RhCl(CO)₂]₂. The *cis* relationship of the carbonyl groups follows from the observation of two sharp M–CO stretching bands in the solution phase infrared spectra, cf. Table 2.

Synthesis of bimetallic materials is quite facile with rhodium carbonyls. Thus, either (phenazine)Rh(CO)₂Cl or (phenazine) [Rh(CO)₂Cl]₂ (**14**), can be obtained from phenazine and [Rh(CO)₂Cl]₂ by adjusting the ratio of the starting materials. The ¹³C NMR spectrum of **11** displayed two doublets at 182.7 and 179.5 ppm with *J*(¹³C–¹⁰³Rh) of 70 and 72 Hz respectively. The ¹H and ¹³C NMR spectra of the new rhodium carbonyl phenazine complexes were very similar to those of the corresponding platinum compounds [5] and were assigned by analogy. Although infrared spectroscopy shows that chloroform solutions of **14** do not contain a detectable amount of [Rh(CO)₂Cl]₂, both ¹H and ¹³C NMR spectra provide evidence for a dynamic process. The signals due to H(1) and H(4) are broad and coupling with the *ortho*-protons is lost. In addition, the carbonyl carbon peak is broad and does not exhibit ¹⁰³Rh–¹³C coupling. The most likely explanation of these spectral features is a rapid cleavage of one of the Rh–N bonds in an equilibrium which strongly favors the dirhodium species.

A particularly interesting dirhodium compounds is (pyrazine)[Rh(CO)₂Cl]₂ (**15**), also reported by Balch and coworkers [6]. In solution, **15** is light yellow but the microcrystalline solid is deep purple with λ_{max}(Nujol) at 300, 375, 415 and 650 nm. The electronic spectrum is, with the exception of the longest wavelength band, quite similar to that of (phenazine)[Rh(CO)₂Cl]₂. In **14**, however, nonbonded repulsions between the phenazine peri-protons and the chloride and carbonyl ligands cause the coordination plane of the rhodium atoms to twist to that it is approximately perpendicular to that of the phenazine rings. In this conformation, the molecule is quite bulky and has little opportunity for intermolecular interaction. In **15**, the heterocyclic ligand has no peri-hydrogen atoms and molecular models indicate that the two Rh(CO)₂Cl planes can be coplanar with pyrazine. The molecule is thus flat and able to stack so that one rhodium (I) site lies over another. We have not yet established whether there exists in (pyrazine)[Rh(CO)₂Cl]₂ a slipped stack packing with one

(pyrazine)Rh₂ unit translated with respect to another or whether the (pyrazine)Rh₂ units are cofacial so that a double string of Rh–Rh bonds runs through the lattice. In any event, the 650 nm absorption, for which we estimate the extinction coefficient to be about 4×10^4 , is quite similar to that found by Gray and Mann for rhodium(I) complexes in which the metals are held in close proximity by bridging isocyanides [7].

Treatment of **15** with excess iodine produces black (pyrazine)[Rh(CO)₂Cl]₂I_{4.2} (**16**). The infrared spectrum of this nonconducting solid showed $\nu(\text{CO})$ at 2015 and 2105 cm⁻¹, indicating that the rhodium remains in the +1 oxidation state. Also, the ring breathing modes in the coordinated pyrazine are essentially unchanged so that ring iodination of the pyrazine is unlikely to have occurred. The resonance Raman spectrum displays a band at 160 cm⁻¹ due to I₅⁻. It thus seems most probable that **16** is a partially oxidized derivative of **15** in which an electron has been removed from an orbital which is predominantly ligand-centered, as, for example, in *cis*-(phenoselenazine)₂PtCl₂I_{3.9} [1].

Redox chemistry

Cyclic voltammetry (Table 6) of (phenazine)Rh(CO)₂Cl in dichloromethane reveals that reduction occurs at -0.85 V (relative to SCE reference); $i_p(\text{red})/i_p(\text{ox})$ is ~ 1.2, indicating that the reduction product undergoes gradual decomposition in solution. An irreversible second reduction wave occurs at -1.35 V. Electrochemical

TABLE 6
CYCLIC VOLTAMMETRY DATA

| Compound | Peak potential (mV) ^{a,b} | $E_{\text{ox}} - E_{\text{red}}$ (mV) ^c |
|---------------------------------------|------------------------------------|--|
| 5 | 1.2(i) | 100 |
| | 0.95(i) | |
| | -1.0(i) | |
| | -1.32 | |
| 6 | 1.05(i) | 70 |
| | -0.94 | |
| | -1.3(i) | |
| 9 | 1.02(i) | 120 |
| | -1.05 | |
| | -1.32(i) | |
| 10 | 0.65(i) | |
| | -1.3(i) | |
| 11 | -0.75 | 90 |
| | -1.22 | 100 |
| 13 | -0.71 | 120 |
| | -1.36(i) | |
| 14 | -0.28 | 75 |
| | -0.75 | 95 |
| | -1.22 | 100 |
| (pyridine)RhCl(COD) no waves observed | | |

^a In CH₂Cl₂ containing 0.1 M (C₄H₉)₄NBF₄ supporting electrolyte. ^b Potential relative to SCE. *i* refers to no reverse wave. ^c At 100 mV/sec scan rate.

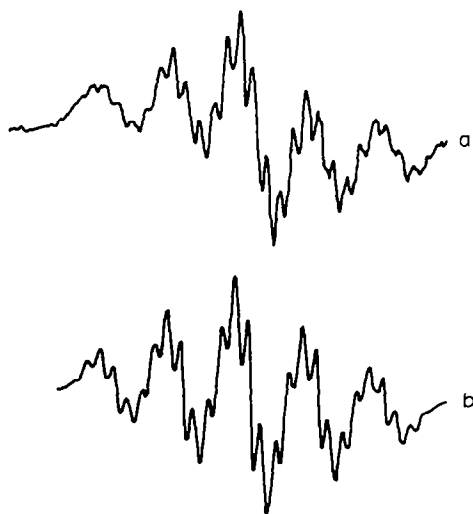


Fig. 1. Observed (a) and calculated (b) X-band EPR spectrum of (phenazine)Rh(CO)₂Cl⁻. The simulated spectrum uses Lorentzian curves with a width of 0.6 G.

reduction of **11** at -0.85 V was carried out in a cell positioned in the cavity of an EPR spectrometer. The spectrum of the anion radical (phenazine)Rh(CO)₂Cl⁻ (**17**), thus produced comprises a complex multiplet centered at $g = 2.0046 \pm 0.0005$ and is shown in Fig. 1, along with the simulated spectrum. Optimized fitting of the observed and calculated spectra using two equivalent ¹⁴N nuclei and three pairs of equivalent protons provided the hyperfine coupling parameters $A(^{14}\text{N})$, 6.82 G ; $A(\text{H}(1))$, 1.70 G ; $A(\text{H}(2))$, 1.35 G ; and $A(\text{H}(3))$, 1.0 G. These data may be compared with the hyperfine splittings $A(\text{N})$, 5.14 G ; $A(\text{H}(1))$, 1.92 G, and $A(\text{H}(2))$, 1.61 G in phenazine anion radical [8]. No evidence of ¹⁰³Rh hyperfine coupling was observed and so we believe that the LUMO in (phenazine)Rh(CO)₂Cl is very largely centered on the heterocyclic ligand, as is the HOMO in (pyrazine)[Rh(CO)₂Cl]₂. Similarly, no ¹⁰³Rh splitting was observed by Crosby et al. in Rh(bipyridyl)(norbornadiene)⁻ for which $a(\text{N}) = 2.5$ G and $a(\text{H}) = 2.5$ G for four protons were reported [9]. Reversible cyclic voltammograms were also obtained for **10** and **13** but the radicals formed appear to be too short lived to obtain useful EPR data. Reduction of **11** at the potential of the second wave produced phenazine anion radical, which was identified by its EPR spectrum.

A complicated redox sequence was observed in the reaction of (phenazine)Rh(CO)₂Cl with chloroplatinic acid in methanol. At room temperature, the Rh-N bond is readily cleaved to form yellow (phenazinium)₂PtCl₆ (**18**), which crystallizes from the reaction mixture. Its infrared spectrum displays bands at 3470 and 325 cm⁻¹ due to N-H and Pt-Cl stretching respectively and matches the spectrum of the salt prepared by metathesis of phenazinium chloride with PtCl₆²⁻. Infrared analysis of the liquid from which **18** separated reveals strong bands at 2110 and 2040 cm⁻¹. The former band is assigned to Rh(CO)Cl₄⁻, for which a CO stretching frequency of 2111 cm⁻¹(s) has been reported [10]. The 2040 cm⁻¹ band remains unassigned but it is clear that no Rh(CO)₂Cl(CH₃OH), $\nu(\text{CO})$ 2070 and 2000 cm⁻¹, is formed.

When (phenazine)Rh(CO)₂Cl and chloroplatinic acid are heated in methanol, reduction of phenazine to dihydrophenazine occurs and red, microcrystalline *trans*(dihydrophenazine)₂PtCl₂, (**19**) separates. The infrared spectrum of **19** shows N–H and Pt–Cl stretching bands at 2800(br) and 310 cm⁻¹. In the ¹H NMR spectrum in dimethyl sulfoxide, the only solvent found suitable for NMR experiments, the ring protons appear as an *AA'BB'* multiplet with δ(*A*) 8.00 and δ(*B*) 8.29; the N–H proton appears as a broad singlet at 8.83 ppm and so it is likely that **19** dissociates in solution. X-ray photoelectron spectroscopy (XPS) proved helpful in characterizing these platinum compounds. The formal oxidation state of platinum in **18** is unambiguously +4 and in this compound, the Pt(4*f*_{5/2}) and 4*f*_{7/2} binding energies are 76.0 and 72.8 eV. These core levels shift to 78.5 and 75.1 eV in **19**, consistent with reduction of platinum(IV) to platinum (II). In both compounds, the nitrogen 1s levels are split into doublets at 399.7 and 401.5 eV. The XPS peak at higher energy is assigned to nitrogen bonded to H⁺ or platinum(II) as the electron-withdrawing effect of these groups should raise the N(1s) binding energy. Less electronegative Rh(I) has a smaller effect on the N(1s) energies and the degenerate nitrogen binding energies in **11** and **14** are 399.8 and 400.8 eV respectively. The Rh(3*d*_{5/2}) levels in both were 309.6 eV relative to C(1s) at 285.0 eV. Because pure **18** is stable in refluxing methanol, it is probable that the platinum is being reduced by the rhodium(I) initially present. The source of the hydrogen atoms incorporated into the dihydrophenazine ligand is the methanol and, when carried out in the CH₃OD solvent, *trans*-(dideuterophenazine)₂PtCl₂, **20**, ν(N–D) 2150 cm⁻¹, was obtained. ¹H NMR and infrared analysis of **20** indicates that deuterium is not incorporated into the carbocyclic ring positions.

Experimental

Heterocyclic ligands used in this study were obtained from the Aldrich Chemical Company and used without further purification. Infrared spectra were recorded on Nujol mulls. NMR spectra were obtained on Varian XL-100 and XL-200 instruments using internal (CH₃)₄Si as a reference and CDCl₃ solvent.

(Phenazine)RhCl(C₈H₁₂) (**1**). To 1.25 g (2.5 mmol) [RhCl(COD)]₂ in 30 ml acetonitrile was added 0.90 g (5.0 mmol) phenazine in a minimum amount of warm acetonitrile. Needle crystals began to separate from the orange solution and, after 0.5 h, they were collected on a filter, washed with fresh solvent and vacuum dried. The yield was 1.6 g (75%).

An 0.8 g portion of this product was dissolved in boiling acetonitrile. Upon cooling, the solution deposited 0.48 g of α-(phenazine)RhCl(COD) as fine, brown needles. On standing, there separated from the mother liquor 0.05 g of the β form as red-brown plates. Infrared spectra and analyses for carbon, hydrogen and nitrogen for the crude product and for both crystalline forms were essentially the same.

(Phenazine)IrCl(C₈H₁₂) (**6**). Cyclooctadieneiridium(I) chloride dimer was prepared from hydrated IrCl₃ according to the method of King [11] for the rhodium analogue. A 0.95 g sample of this crude dimer was dissolved in 250 ml methylene chloride and the solution filtered. Phenazine, 0.51 g (2.8 mmol), was added. The resulting orange solution was evaporated to a small volume under reduced pressure and diluted with ethanol. On cooling to –20°C, 0.8 g of red-brown powder separated. This was recrystallized from hot acetonitrile to give 0.20 g of the pure iridium complex as dark brown needles.

(*Quinoxaline*)*RhCl*(C_8H_{12}) (**9**). Quinoxaline, 1.66 mmol in 2 ml acetonitrile, was added to a solution of 0.41 g (0.83 mmol) $[RhCl(COD)]_2$ in 20 ml of the same solvent. The mixture was evaporated to ca. 2 ml with a nitrogen jet. Yellow flakes and yellow nodules separated. The solution was heated to boiling and filtered. On cooling, the product separated as yellow nodules which were filtered off and vacuum dried, yield 0.2 g (32%).

(*Phenazine*)*Ir*(CO)₂*Cl* (**13**). A mixture of 0.31 g $[Ir(CO)_3Cl]_n$, 0.18 g phenazine and 25 ml acetonitrile was stirred under reflux for 8 h, filtered and the filtrate evaporated. Unreacted phenazine was removed from the residue by vacuum sublimation at 80°C. Recrystallization from toluene/heptane provided 0.05 g of yellow crystalline product m.p. 195°C (dec.).

(*Phenazine*)*RhCl*(CO)₂ (**14**). A solution of 0.36 g (2 mmol) phenazine in 10 ml benzene was added dropwise to 0.4 g (1mmol) resublimed $[RhCl(CO)_2]_2$ in 35 ml benzene. The resulting orange solution was evaporated to ca. 3 ml under reduced pressure and diluted with hexane to give 0.60 g (80%) of product as yellow needles.

(*Phenazine*) $[RhCl(CO)_2]_2$ (**15**). This bimetallic compound was prepared using half the amount of phenazine as in the above experiment. The yield of orange, crystalline material was 0.45 g (79%).

(*Pyrazine*) $[Rh(CO)_2Cl]_2I_{4,2}$ (**16**). A 0.245 g sample of (pyrazine) $[Rh(CO)_2Cl]_2$ was treated with iodine vapor at 50°C using the apparatus previously described [1]. Iodine consumption proceeded over the course of 4 days during which time, the purple starting compound became black. Unreacted and absorbed iodine was removed by pumping at a nominal pressure of 3×10^{-6} mm. The yield of product was 0.500 g.

Reaction of (PNZ)*Rh*(CO)₂*Cl* with $H_2PtCl_6 \cdot 3H_2O$. A 0.30 g sample of the rhodium complex was dissolved with gentle warming in 20 ml methanol. After cooling to room temperature, 0.40 g $H_2PtCl_6 \cdot 3H_2O$ in 10 ml methanol was added. The mixture was stirred for 0.5 h and then, the golden colored needles which had separated were collected on a filter, washed with fresh solvent and vacuum dried. The yield of (HPNZ)₂PtCl₆ (**18**) was 0.26 g.

trans-(H_2PNZ)₂PtCl₆ (**19**). A mixture of 0.61 g (PNZ)*Rh*(CO)₂*Cl* and 1.0 g $H_2PtCl_6 \cdot 3H_2O$ in 25 ml methanol was refluxed and stirred for 1.5 h. The hot reaction mixture was filtered and the dark red microcrystals were washed with warm methanol, then vacuum dried, to provide 0.36 g of **19**.

X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950B spectrometer using monochromatized Al- K_{α} X-rays (E 1486.6 eV). Data were accumulated on a HP 21MX computer and plotted in digital form. The C(1s) photoelectron line was taken as an internal standard with E_b 285.0 eV.

Thermal desorption experiments were carried out on a Dupont 21-491B GC/MS instrument incorporating a Varian 2740 GC and a Dupont 21-094 data system. Samples weighing between 3 and 10 mg were placed in sample holders consisting of 10 cm lengths of glass tubing plugged at each end with solvent-extracted and oven dried glass wool. For each run, a sample tube was coupled into the GC flow path in the column oven just ahead of the detector. A 2 m length of 1/8" o.d. stainless steel tubing for equilibrating incoming helium to the oven temperature connected the sample tube to the injection port. After a preliminary sample flush with helium at 30°C, the temperature of the GC oven was raised to 350°C at a rate of 10°C/min. The flowing helium swept the desorbed gases into the mass spectrometer via a single

stage glass jet helium separator. Mass spectra were recorded every 60 seconds. A blank run with the empty sample tube was made before each sample run, and the data were stored in the same file with the sample data to facilitate blank corrections. Blanks were negligible in each run reported here.

References

- 1 A.R. Siedle, M.C. Etter, M.E. Jones, G. Filipovich, H.E. Mishmash and W. Bahmet, *Inorg. Chem.*, 21 (1982) 2624
- 2 G.A. Swan and D.G. Felton, *Phenazines*, Interscience Publishers, New York, N.Y., 1957.
- 3 A.J. Pribula and R.S. Drago, *J. Am. Chem. Soc.*, 98 (1976) 2784.
- 4 In (4-methylpyridine)PtCl₂(C₂H₄), the pyridine ring orientation appears to be determined by both steric and electronic factors. The dihedral angle between the ring and the PtCl₂N plane is 49.7°, F. Caruso, R. Spagua and L. Zambonelli, *J. Cryst. Mol. Struct.*, 8 (1970) 47.
- 5 R.A. Newmark and A.R. Siedle, manuscript in preparation.
- 6 A.L. Balch and R.D. Cooper, *J. Organometal. Chem.*, 169 (1979) 97.
- 7 K.R. Mann, J.A. Thich, R.A. Bell, C.L. Coyle and H.B. Gray, *Inorg. Chem.*, (1980) 19 2462 and refs. cited therein.
- 8 A. Carrington and J. Dos Santos-Veiga, *Mol. Phys.*, 5 (1962) 21.
- 9 W.A. Fordyce, K.H. Pool and G.A. Crosby, *Inorg. Chem.*, 21 (1982) 1027.
- 10 M.J. Cleare and W.P. Griffith, *J. Chem. Soc. A*, (1970) 2788.
- 11 R.B. King, *Organometallic Syntheses*, Academic Press. New York, N.Y., 1965, p. 132