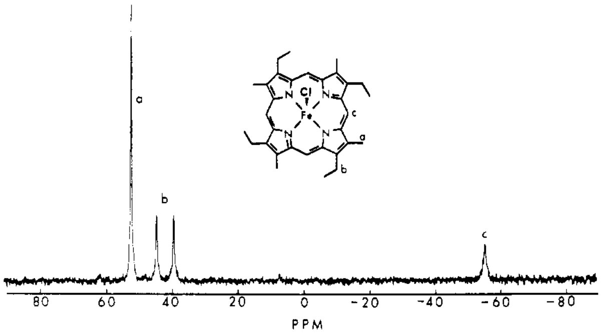

Figure 1. Deuterium NMR spectrum at 55.28 MHz of the chloroiron(III) etioporphyrin complex deuterated by the *o*-dichlorobenzene reflux procedure: $CDCl_3$ solvent, 25 °C, referenced to $(CD_3)_4Si$. The methylene deuterons are diastereotopically inequivalent due to the out-of-plane iron atom.

positions. The primary and secondary ring-adjacent positions were equally deuterated. Eight days of reflux produced the same level of deuteration at the methine position, but the ring methyl and methylene groups were 60% deuterated. The recovery of porphyrin was 84%. Integrity of the porphyrin is demonstrated by the deuterium NMR spectrum in Figure 1 in which case the chloroiron(III) etioporphyrin complex was prepared from deuterated porphyrin via a literature method.[11] Proton NMR assignments for this species have been made previously.[12,13] In addition to being prepared from the sodium salt, the deuterated *p*-toluenesulfonic acid can be prepared by addition of deuterium oxide to the acid followed by rotoevaporation to dryness. Acid prepared in this manner did not yield any detectable deuterium exchange at the methine or the ring-adjacent positions by the *o*-dichlorobenzene reflux method. Addition of 1 equiv of finely powdered sodium chloride gave results identical with those obtained when starting with the sodium salt of the acid. Surprisingly, it is apparent that sodium chloride serves an essential role in the exchange reaction.

An alternate more convenient procedure may be employed for methine deuteration. For the melt procedure 2 g of *p*-toluenesulfonic acid monohydrate was dissolved in 10 mL of deuterium oxide, the solution was rotary evaporated to dryness, and the residue was vacuum dried at 60 °C for 3 h. To the deuterated acid was added 25 mg of etioporphyrin and the mixture was fused under nitrogen at 120 °C. The porphyrin was precipitated by pouring the hot melt into 80 mL of 0.01 M aqueous sodium hydroxide. After removing the porphyrin by filtration, it was redissolved in chloroform and precipitated by addition of heptane. The product was found to be 83% methine deuterated after a 9-h melt, and no ring-adjacent deuteration was detected.[14]

The deuteroacetic acid procedure[4] mentioned above was investigated to determine the generality of this previously unnoticed phenomenon of ring-adjacent exchange. Refuluxing etioporphyrin in deuterioacetic acid for 24 h produced ~3% deuteration at the ring-adjacent methyls and ~0.5% at the ring-adjacent methylenes. Sealed-tube reactions produced 90% deuteration of the ring-adjacent methyls and 45% deuteration of the ring-adjacent methylenes after 8 days at 180 °C, but 40% of the porphyrin was degraded under these conditions.

No exotic role need be postulated for the sodium chloride essential to the ring-adjacent exchange procedure with *p*-toluenesulfonic acid. Toluenesulfonic acid was found to degrade in fusion reactions conducted above 160 °C. Considering this and the fact that even methine detueration was not observed in the absence of sodium chloride, it would seem that the salt must enhance the solubility of the extremely hydrophilic acid in refluxing *o*-dichlorobenzene. In the absence of salt the acid evidently forms a separate phase and is degraded at the reflux temperature of 180 °C.

It has previously been established that methine deuteration proceeds via electrophilic aromatic substitution of the free base porphyrin.[4] On the other hand, exchange of the ring-adjacent positions with deuterioacetic acid proceeds via deprotonation of the ring-adjacent position, with the porphyrin most likely in the dication form. Studies of the base-promoted exchange of benzylic hydrogens show that the exchange rate is 9 times greater for toluene than it is for ethylbenzene.[15] This may be compared with the 6-fold greater rate observed for the ring-adjacent primary vs. the ring-adjacent secondary positions with deuteroacetic acid and contrasted with the nearly equivalent rates of substitution for these two positions with the *p*-toluenesulfonic acid system. For a free radical mechanism the rate would be greater at the secondary than at the primary ring-adjacent position. We thus suggest that both a free radical and deportonation mechanism are at work, and the result is approximately equal rates of deuteration of the two positions.

In summary, we have shown that acid-catalyzed exchange potentially produces deuterium substitution at ring-adjacent alkyl moieties as well as at methine positions in octaalkylporphyrins. Combination of these procedures and a corresponding back-exchange technique allows selective deuteration of these compounds at the ring-adjacent and/or methine positions as well as preferential deuteration of the primary vs. secondary ring-adjacent positions.

Acknowledgment. Support from National Science Foundation Grant CHE-82-09398 is gratefully acknowledged. The Bruker WM-360 NMR spectrometer was purchased in part with National Science Foundation Grant CHE 82-01836.

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[14] Recovered acid showed exchange of phenyl positions ortho to the methyl. Use of acid deuterated at this position produced quantitative deuteration of the methine positions in 90 min at 150 °C (toluenesulfonic acid deuterated at these positions may be obtained by recycling acid from previous fusions or synthesized from deuteriotoluene).

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Iridium, Platinum, and Palladium Complexes of Some New Hybrid Aminophosphine Ligands. A Chelate-Assisted N-H Oxidative Addition to Iridium(I) and the Structural Characterization of a Novel Ortho C-Metalated Platinum(II) Complex

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The insertion of a transition-metal complex into an N-H bond is a reaction of potential synthetic utility for the directed catalytic functionalization of ammonia and amines.[2] Nevertheless, documented examples of the oxidative addition of a N-H bond are

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[1] (a) Tulane University. (b) University of Delaware.

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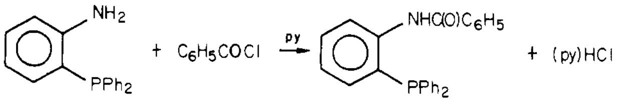
rare. The addition reactions of imides,[3] tetrazoles,[4] pentafluoroanilines,[5] and ammonium ion[6] to platinum(0), rhodium(I), and iridium(I) have been classified as protonation reactions,[7] but the only examples involving N–H addition of ammonia or simple amines appear to be with $Os_3(CO)_{12}$.[8] In order to promote this reaction we have synthesized some new hybrid phosphine–amine(amide) ligands which can undergo intramolecular chelate-assisted N–H oxidative addition.[9] This communication reports the first example of iridium(I) insertion into a N–H bond and the synthesis and structural characterization of a novel ortho C-metalated platinum(II) complex which is formed from a platinum(II) precursor by a C–H oxidative addition and N–H reductive elimination sequence.

Reaction of 1 equiv of benzoyl chloride with *o*-(diphenylphosphino)aniline[10] in the presence of pyridine in dry THF under nitrogen[11] gives *o*-(diphenylphosphino)-*N*-benzoylaniline (PNH(CRO)) (R = Ph) (eq 1).[12] Using similar techniques we have

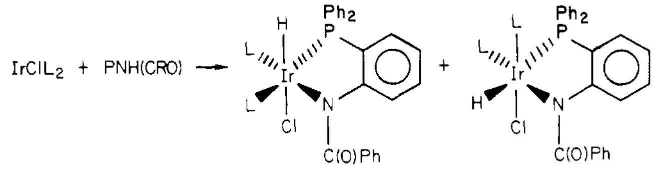


PNH(CRO)

(1)

prepared *o*-(diphenylphosphino)-*N*-benzylaniline (PNHR), *o*-(diphenylphosphino)-*N*-phenylbenzylamine (PCNHR), and *o*-(diphenylphosphino)-*N*-phenylbenzamide (P(CO)NHR).

Addition of 1 equiv of PNH(CRO) in oxygen-free dry toluene to a toluene solution of $IrClL_2$ ($L_2 = 2PPh_3$ (a), dppe (b))[13] under nitrogen at 25 °C gives an isomeric mixture of the amido hydride iridium(III) complexes I and II (eq 2). These oxygen-sensitive



I II

(2)

complexes are soluble in polar organic solvents. The isomers (Ia:IIa = 2.4:1, Ib:IIb = 1.5:1 by ^1H NMR) are not separable by chromatography. Isomer I has hydride trans to chloride and three magnetically inequivalent phosphines cis to hydride.[14]

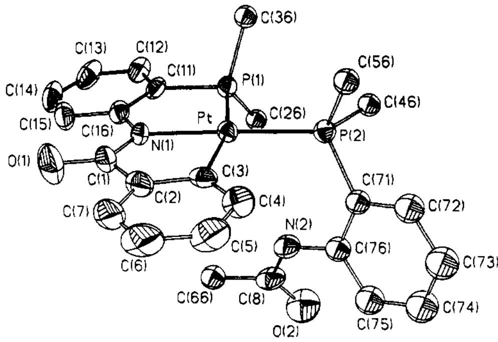
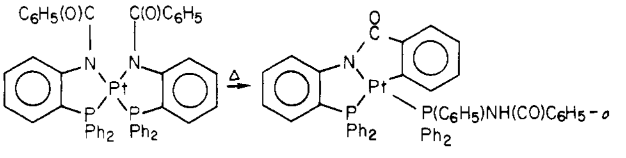


Figure 1. ORTEP diagram for VII. Terminal phenyl groups shown as pivotal atom only. Pt–P(1), 2.298 (2); Pt–P(2), 2.259 (2); Pt–N(1), 2.063 (7); Pt–C(3), 2.065 (8) Å. P(1)–Pt–P(2), 100.6 (1)°; P(1)–Pt–N(1), 83.7 (2)°; P(1)–Pt–C(3), 164.8 (3)°; P(2)–Pt–N(1), 175.6 (2)°; P(2)–Pt–C(3), 94.5 (3)°; N(1)–Pt–C(3), 81.2 (3)°.

Isomer II has hydride trans to one phosphorus and cis to two phosphorus atoms. Amido nitrogen coordination causes the expected low-energy shift in ν_{CO} from 1680 cm^{-1} in the free ligand to 1595 cm^{-1} in Ia and IIa and 1590 cm^{-1} in Ib and IIb. Furthermore, amide II and III IR absorptions (coupled δ_{NH} and ν_{CN} at 1510 and 1300 cm^{-1} in free ligand) disappear, but new ν_{CN} bands appear in the complexes at 1360 (Ia, IIa) and 1335 cm^{-1} (Ib, IIb).[15] These compounds represent only the second report of Ir(III) amido complexes.[16] The selectively deuterated compound PND(CRO) (ν_{ND} = 2480 cm^{-1}) has been prepared from PNH(CRO) by using 1 equiv of *n*-BuLi followed by D_2O. Treating $IrCl(PPh_3)_2$ with PND(CRO) yields $IrDCl[PN(CRO)](PPh_3)_2$. The band due to ν_{ND} is lost but bands for ν_{IrD} calculated to be at 1563 and 1429 cm^{-1} are obscured by strong ligand bands. By contrast, reaction of $IrCl(PPh_3)_2$ with 1 equiv of a 1:1 mixture PPh_3/benzanilide, or PPh_3/benzamide, or with 1 equiv of benzanilide, or benzamide, does not give iridium(III) hydrides.

The ligand PNH(CRO) gives new platinum(II) and palladium(II) complexes by sequential N–H and C–H oxidative additions and reductive eliminations. Treating K_2PtCl_4 with PNH(CRO) gives *trans*-$PtCl_2[PNH(CRO)]_2$ (III).[17] Refluxing III with triethylamine in acetonitrile under nitrogen gives the amido complex *cis*-$Pt[PN(CRO)]_2$ (V) via the $^{31}P\{^1H\}$ NMR detected intermediate IV. A trans to cis stereochemical change occurs on conversion of III to IV, and we propose that this is induced by coordination of a deprotonated amide nitrogen.[18] Addition of HCl to V gives the cis isomer VI (Scheme I). Prolonged reflux (ca. 2 h) of V in acetonitrile, benzene, or chloroform yields the diamagnetic, ortho-metalated complex VII (eq 3). The structure



VI VII

(3)

of VII has been determined by X-ray crystallography (see Figure 1).[19]

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[12] All formulations are consistent with microanalysis results, conductivity measurements, and IR and NMR spectral data. These are available as supplementary material.

[13] Generated in situ from $[IrCl(C_8H_{14})_2]_2$ and tertiary phosphine; see: van der Ent, A.; Onderelinden, A. L. *Inorg. Chim. Acta* **1973**, *7*, 203–208.

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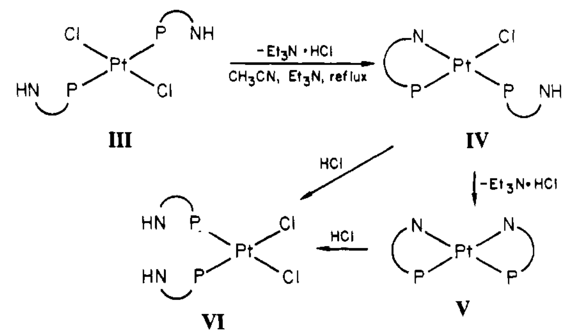
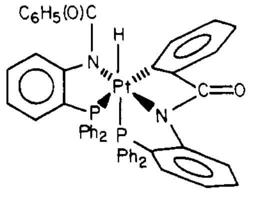
Scheme I[a]



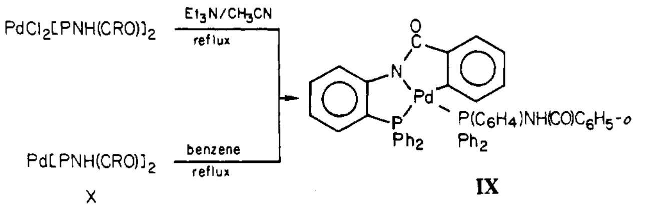
[a] $\widehat{P\,NH} = o\text{-}Ph_2PC_6H_4NHC(O)C_6H_5$; $\widehat{P\,N} = o\text{-}Ph_2PC_6H_4NC(O)C_6H_5^-$.

o-$Ph_2PC_6H_4NHC(O)C_6D_5$ has been prepared from o-$Ph_2PC_6H_4NH_2$ and C_6D_5COCl. Isolation of VII using this ligand yields a product deuterated at nitrogen (ν_{ND} 2260 cm^{-1}). This result suggests conversion of V to VII via C–H addition followed by N–H reductive elimination from the platinum(IV) hydride intermediate VIII.[7,20]



VIII

The palladium analogue IX is formed in high yield from



$PdCl_2[PNH(CRO)]_2$ and Et_3N in acetonitrile. Alternatively, IX can be prepared by refluxing a benzene suspension of the complex $Pd[PNH(CRO)]_2$ (X).

Acknowledgment. We thank B. Brammel (U.N.O.) for ^1H NMR measurements and U. Geiser (W.S.U.) for magnetic measurements. We thank the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE-820882, for the 360-MHz ^1H NMR spectrum. The University of Delaware received support from the National Science Foundation for the purchase of the diffractometer.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates for VII, and microanalytical and IR and NMR spectral data for all new compounds (41 pages). Ordering information is given on any current masthead page.

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(19) For VII: space group $P\bar{1}$, a = 12.038 (3) Å, b = 12.576 (5) Å, c = 16.220 (6) Å, α = 105.80 (3)°, β = 104.84 (3)°, γ = 95.75 (3)°, V = 2245.6 (13) Å^3, Z = 2. The structure was solved by standard heavy-atom methods and after correction for absorption was refined by blocked-cascade procedures (SHELXTL 4.1) with anisotropic temperature factors and rigid-body constraints on the terminal phenyl rings (5115 reflections, $3\sigma(F)$ cutoff). R_F = 3.75%, R_{wF} = 4.02%. A severely disordered, substoichiometric (site occupation ~20%) molecule of $CHCl_3$ was found and refined.

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Highly Reduced Organometallics. 17. Synthesis, Isolation, and Characterization of Hydridopentacarbonylmetalate(2−) Anions of Vanadium, Niobium, and Tantalum: $HM(CO)_5{}^{2-}$

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Compounds of the general formula $HM(CO)_x{}^{2-}$ have been postulated to be key intermediates in the reactions of carbonylmetalate trianions, $M(CO)_x{}^{3-}$, with Brønsted acids, but very little evidence for their existence has been presented previously.[2,3] In this communication, the isolation and characterization of monoprotonated derivatives of the carbonyl trianions of vanadium, niobium, and tantalum are described. These are the first examples of hydrides containing transition metals in formally negative oxidation states. Their synthesis also provides important additional evidence for the existence of unprotonated carbonyl trianions since the latter have been previously characterized mainly on the basis of their derivative chemistry.[2,4] It is well established that carbonyl hydrides and their conjugate bases often cannot be distinguished reliably on this basis.[5]

Treatment of the red to deep red ammoniacal solutions of $Na_3[M(CO)_5]$ (M = V,[2] Nb,[4] and Ta[4]) dropwise with 1 equiv of ethanol in THF at −70 °C over a period of 5 min provided orange to red-orange solutions. Addition of 3 equiv of $[Et_4N][BH_4]$ at −70 °C resulted in the rapid precipitation of 60–80% yields of microcrystalline bright yellow (**1**, V), orange (**2**, Nb), or orange-red (**3**, Ta) products. These air-sensitive solids provided satisfactory elemental analyses for unsolvated $[Et_4N]_2[HM(CO)_5]$ without further purification.[6] Infrared spectra for compounds **1**–**3**[7] were qualitatively very similar to those of the corresponding triphenylstannyl substituted dianions, $[Et_4N]_2[Ph_3SnM(CO)_5]$.[2,4] However, it was necessary to obtain NMR spectra of these substances to exclude alternative formulations such as $[Et_4N]_4[M_2(CO)_{10}]$. These spectra had to be obtained for the thermally unstable disodium salts, $Na_2[HM(CO)_5]$, in *liquid ammonia* at −50 °C because of facile decomposition of compounds **1**–**3** in polar solvents at room temperature and their poor solubility at low temperatures. The ^1H NMR spectrum for $Na_2[HTa(CO)_5]$ exhibited a fairly sharp singlet ($\Delta\nu_{1/2}$ = 30 Hz) at −2.23 ppm which is compatible with previous values reported for the isoelectronic species $HW(CO)_5{}^-$ (−4.2 ppm)[8] and $HRe(CO)_5$ (−5.7 ppm).[9] Initial attempts to detect the hydride resonance of $Na_2[HNb(CO)_5]$ were unsuccessful.[10]

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(7) Nujol mull spectra in ν(CO) region for **1**: 1905 w, 1700 s, br. **2**: 1923 w, 1700 s, br. **3**: 1922 w, 1700 s, br. Metal–hydride stretching frequencies have not been identified for these compounds.

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