action with the tetra-*n*-butylammonium cation, producing nearly quantitative amounts of *trans*-[PtH(Cl)(PEt_3)$_2$] (Scheme I).

The presence of NBu_3, a product of the Hoffman elimination, was detected by GC analysis of the electrolyzed solution, and comparison of the peak area with that of standard samples showed formation of one equivalent of NBu_3 for each equivalent of *cis*-[$PtCl_2(PEt_3)_2$] precursor. Since the reduction is performed under a continuous argon purge, detection of but-1-ene was not possible. The reaction of [$Pt(PEt_3)_2$] with the β-C–H bonds of TBAP must occur quite rapidly since by the end of the electrolysis the air-stable complex *trans*-[PtH(Cl)(PEt_3)$_2$] has been formed.[7]

When the electrolysis is performed in the presence of small amounts of purposely added water (vide supra) and in the absence of activated alumina, then the amount of *trans*-[PtH(Cl)(PEt_3)$_2$] obtained is decreased (although this is still the major platinum-containing product) and the reaction pathway is diverted to an alternate route leading to the formation of acetamide. In this case, [$Pt(PEt_3)_2$] acts as a base promoting the reaction between water and acetonitrile.[10–12] Any possible heterogeneous mechanisms for acetamide formation are ruled out by the fact that the electrolysis takes place in the presence of liquid mercury, a poison for heterogeneous systems.[13]

The preference of [$Pt(PEt_3)_2$] to act as a base is quite marked. Substrate molecules for trapping or oxidative addition reactions must be added prior to electrolysis since by the end of the electrolysis, most of the [$Pt(PEt_3)_2$] has already reacted to form *trans*-[PtH(Cl)(PEt_3)$_2$]. We were able to trap a small amount of the unreacted [$Pt(PEt_3)_2$] by the addition of 1 equiv of PhC≡CPh immediately after the electrolysis.[14] Although the major product was still *trans*-[PtH(Cl)(PEt_3)$_2$], 22% of the platinum-containing species, estimated from peak heights in the $^{31}P\{^1H\}$ NMR spectrum, was a new complex with NMR data (δ_P 11.8 ($^1J_{Pt-P}$ = 3299 Hz)) typical for a compound of the type [Pt(PhC≡CPh)(PEt_3)$_2$]. Even with 5–10 equiv of oxidative addenda (i.e., PhCN, PhCl) for each equivalent of the *cis*-[$PtCl_2(PEt_3)_2$] precursor added prior to the electrolysis, the reduced complex still reacts as a base via the Hoffman elimination reaction rather than undergoing oxidative addition. We have found that only when the concentration of oxidative addenda greatly exceeds that of TBAP will [$Pt(PEt_3)_2$] oxidatively add small molecules (such as those mentioned above). Studies into the exploitation of this chemistry as a new synthetic method are currently in progress. When TBAP is replaced by a nonprotic background electrolyte (i.e., $NaClO_4$), a small amount of *trans*-[PtH(Cl)(PEt_3)$_2$] is formed, presumably from the reaction of [$Pt(PEt_3)_2$] with the mildly acidic C–H bonds of acetonitrile (pK_a = 25),[15] but decomposition to platinum metal is quite extensive, hindering mechanistic studies.

It may not be surprising that products resulting from acid/base chemistry are more readily observed in electrochemical experiments than in photochemical ones.[5,6] In the photochemical experiments, a base such as NaOH must be added to observe acid/base chemistry, such as acetonitrile hydration, due to the generation of the Lewis acid CO_2 from the photolysis of [$Pt(C_2O_4)(PEt_3)_2$].[16]

We have also found that under a different set of reaction conditions, which allow O_2 to enter into the reaction pathway, *trans*-[PtMe(CN)(PEt_3)$_2$][17] is formed through a reaction with the CH_3CN component of the solvent system. Although benzonitrile readily undergoes C–C oxidative addition (vide supra), we find that O_2 is necessary before we observe C–C oxidative addition of acetonitrile. It is possible that two different mechanistic pathways are involved here which are governed by the amount of O_2 present under the reaction conditions. This type of mechanistic diversity has recently been shown in the case of Pt(II) → Pt(IV) oxidative addition reactions.[18] Since an S_N2-type mechanism for the reaction of CH_3CN and [$Pt(PEt_3)_2$] is highly unlikely,[19] it is quite possible that O_2 present in the system allows a free radical nonchain reaction to take place, leading to the observed product *trans*-[PtMe(CN)(PEt_3)$_2$]. An alternative mechanism involving interaction of the substrate with the metal center prior to bond cleavage may be possible for the aromatic substrate benzonitrile.

The reactions of [$Pt(PEt_3)_2$] with organic substrates are of considerable interest since the observed products result from formal C–H bond activation of TBAP and C–C bond activation of CH_3CN and C_6H_5CN. Detailed mechanistic studies of this dichotomy in reactivity are currently underway.

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Registry No. $Pr(PEr_3)_2$, 66916-63-0; *cis*-[$PtCl_2(PEt_3)_2$], 15692-07-6; *trans*-[PtH(Cl)(PEt_3)$_2$], 16842-17-4; $Bu_4N^+ClO_4^-$, 1923-70-2; PhCN, 100-47-0; *trans*-(PrPh(CN)(PEt_3)$_2$], 33914-65-7; PhC<<tbdC Ph, 501-65-5; *trans*-[PtMe(CN)(PEt_3)$_2$], 22289-45-8; CH_3CN, 75-05-8; water, 7732-18-5; acetamide, 60-35-5.

(10) Acetamide was detected by ^{13}C NMR spectroscopy: δ 178.2, 22.1 (in H_2O/CD_3OD).
(11) The formation of acetamide from [$Pt(PEt_3)_3$], H_2O, and CH_3CN has been reported by Otsuka and co-workers; see ref 4.
(12) The formation of acetamide from the reaction of *trans*-[PtH(Cl)(PEt_3)$_2$] with NaOH in 50/50 H_2O/CH_3CN at 80 °C has been reported; see: Trogler, W. C.; Jensen, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 723.
(13) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.
(14) PhC≡CPh has a reduction potential less negative than *cis*-[$PtCl_2(PEt_3)_2$]; therefore, it cannot be added prior to the electrolysis.
(15) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985.
(16) We thank a reviewer for sharing with us these unpublished results.
(17) Identified by $^{31}P\{^1H\}$ NMR spectroscopy: δ_P 13.7 (J_{Pt-P} = 2620 Hz) (in C_6D_6). See: Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700.
(18) Ferguson, G.; Monaghan, P. K.; Parvez, M.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1669.
(19) The displacement of CN^- is said to be unknown during S_N2 processes in organic chemistry; see ref 15.

Iridium Hydride Complexes Formed by the Intramolecular N–H Addition of Hybrid Phosphine Amines to Iridium(I)

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Summary: The complexes [MCl(1,5-COD)]$_2$ react with *o*-$Ph_2PC_6H_4NHR$ to give tetracoordinated complexes MCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHR$) (M = Rh, Ir, R = CH_2Ph; M = Rh, R = Et) where the amine moiety is uncoordinated. Treating IrCl(1,5-COD)(*o*-$Ph_2PC_6H_4NHR$) with $AgClO_4$ gives the bis-chelate complexes [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHR$)]ClO_4 (R = CH_2Ph, Et). Thermolysis of [Ir(1,5-COD)(*o*-$Ph_2PC_6H_4NHCH_2Ph$)]ClO_4 causes C-

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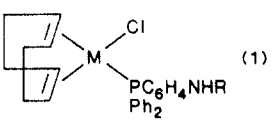
cyclometalation to give $[IrH(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHCH_2C_6H_4)]ClO_4$. Treating $[Ir(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHEt)]ClO_4$ with L (L = py, MeCN) gives $[IrL(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHEt)]ClO_4$, where the amine is uncoordinated. Cyclooctene in $[IrCl(C_8H_{14})_2]_2$ is displaced by $o\text{-}Ph_2PC_6H_4NHR$ to give $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$ (R = CH_2Ph, Et). The deuterated analogue $o\text{-}Ph_2PC_6H_4NDR$ gives the iridium deuteride complex $IrDCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NDR)$.

The insertion of metal centers into an N–H bond is a reaction of strategic importance if one is to develop catalytic reactions involving the homologation of ammonia and amines with alkenes or carbon monoxide. Despite this significance, there is nevertheless little published work to date on such reactions. Examples of insertion reactions where the product amine hydride complex has been isolated or detected are rare, and in such cases the nitrogen moiety is frequently bonded to a strongly electron-withdrawing group.[1] Recently we have used an approach involving intramolecular N–H addition to iridium(I) using a tertiary phosphine moiety as an anchor, and from this work we have successfully achieved N–H addition when the nitrogen is bonded to an electron-withdrawing carbonyl group.[2] We now report that we can use this intramolecular approach to achieve iridium(I) insertion into the unactivated N–H bond of a hybrid phosphine amine ligand.

The compounds used are $o\text{-}Ph_2PC_6H_4NHCH_2Ph$[3] and $o\text{-}Ph_2PC_6H_4NHEt$.[4] These compounds react with $[MCl(1,5\text{-}COD)]_2$ to give $MCl(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHR)$ (M = Rh, R = CH_2Ph, **1a**; M = Rh, R = Et, **1b**; M = Ir, R = CH_2Ph, **1c**) where the amine ligand is uncoordinated (eq 1). Removal of the complexed chloride ligand in **1** by

$$\tfrac{1}{2}[MCl(1,5\text{-}COD)]_2 + o\text{-}Ph_2PC_6H_4NHR \longrightarrow$$



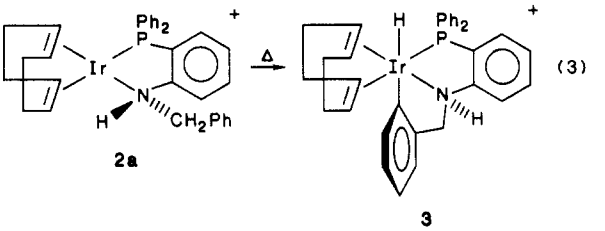
(1)

1

silver ion gives the 14-electron intermediate **2**, which will readily form a bis-chelate complex with the amine ligand. Using this approach with silver perchlorate, we have prepared the cationic iridium(I) complexes $[IrCl(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHR)]ClO_4$ (R = CH_2Ph, **2a**; R = Et, **2b**) (eq 2). These complexes are thermally stable in solution at

$$IrCl(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHR) + AgClO_4 \rightarrow \underset{\mathbf{2}}{[Ir(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHR)]ClO_4} + AgCl \quad (2)$$

ambient temperature and do not undergo N–H addition. Heating solutions of **2b** causes no change, but solutions of **2a** in chloroform at elevated temperature (78 °C) undergo cyclometalation at the benzylic phenyl group to give $[IrH(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHCH_2C_6H_4)]ClO_4$ (**3**) (eq 3).[5] The benzylic hydrogens in the phenyl region are upfield shifted into the δ 6.2–6.6 range.



(3)

2a **3**

The ^1H NMR spectra of **2** show an AB pair multiplicity for the methylenic hydrogens, indicative of nonequivalent nuclei. Since the complexes are dissociated in solution (Λ_M = 12.3 and 13.9 Ω^{-1} cm^2 mol^{-1} for **2a** and **2b**, respectively), the inequivalence is likely due to the diastereotopic methylenic hydrogens. Complex **2b** reacts with pyridine or acetonitrile to give the complex $[IrL(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHEt)]ClO_4$ (L = py, **4a**; L = MeCN, **4b**) (eq 4), where the amine ligand is substituted by L. The sub-

$$\underset{\mathbf{2b}}{Ir(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHEt)^+} + L \rightarrow \underset{\mathbf{4}}{IrL(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NHEt)^+} \quad (4)$$

stitution is confirmed by the upfield shift of the methylenic resonance in the ^1H NMR spectra to δ 3.41 (**4a**) and 3.40 (**4b**) and the observation that these resonances now become magnetically equivalent.

The failure of complex **2** to undergo intramolecular N–H oxidative addition at iridium(I) can be rationalized on the basis that the π-acceptor 1,5-cyclooctadiene ligand causes the iridium(I) center to be insufficiently reactive to such a reaction. This premise finds additional support from previous work which has shown that a similar complex with the more reactive amide, rather than an amine ligand, will undergo such an intramolecular addition.[2] In order to induce a greater basicity at iridium(I), we have now used a cyclooctene complex rather than the 1,5-cyclooctadiene analogue, because this monoene ligand will be more readily displaced by a tertiary phosphine donor. Treating $[IrCl(C_8H_{14})_2]_2$ with 4 mol of $o\text{-}Ph_2PC_6H_4NHR$ gives the hydride complex $IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)$ (R = CH_2Ph, **5a**; R = Et, **5b**) (eq 5).

$$\tfrac{1}{2}[IrCl(C_8H_{14})_2]_2 + 2o\text{-}Ph_2PC_6H_4NHR \rightarrow \underset{\mathbf{5}}{IrHCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NHR)} + 2C_8H_{14} \quad (5)$$

These air-sensitive complexes are thermally stable in CD_2Cl_2 solvent for several hours, although they do slowly halogenate in this solvent if solutions are kept for longer times (the reaction is faster in $CDCl_3$ solvent). When the analogous reaction between $[IrCl(C_8H_{14})_2]_2$ and $o\text{-}Ph_2PC_6H_4NDR$ (R = CH_2Ph, Et) is carried out, the iridium deuteride complex $IrDCl(o\text{-}Ph_2PC_6H_4NR)(o\text{-}Ph_2PC_6H_4NDR)$ (ν(IrD) = 1614 cm^{-1}, ν(ND) = 2395 cm^{-1} (R = Et), ν(IrD) ≈ 1600 cm^{-1} overlapped with aromatic C=C bands, ν(ND) = 2373 cm^{-1} (R = CH_2Ph)) is formed.

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(4) Prepared by reduction of $o\text{-}Ph_2PC_6H_4NHC(O)Me$ (Park, S.; Hedden, D.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1986**, *5*, 1305–1311) with BH_3·THF. Characterized by ν(NH) = 3356 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.5–7.4 (m, 14 H, phenyl), 4.56 (br, 1 H, NH), 3.13 (q, 2 H, CH_2), 1.14 (t, 3 H, CH_3, ^3J(HH) = 7.1 Hz); $^{31}P\{^1H\}$ NMR δ −20.3 (s). Anal. Calcd for $C_{20}H_{20}NP$: C, 78.7; H, 6.60; N, 4.59. Found: C, 78.7; H, 6.65; N, 4.58.

(5) The hydride complex $[IrH(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NDCH_2C_6H_4)]ClO_4$ (ν(ND) = 2396 cm^{-1}) is formed from the deuterio analogue complex $[Ir(1,5\text{-}COD)(o\text{-}Ph_2PC_6H_4NDCH_2Ph)]ClO_4$.