Ruthenated Acetonitrile: Unusual Brønsted Acidity of a Polar "Aprotic" Solvent

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Addition of acetonitrile to the complex [Ru(η^5-indenyl)(PR_2)(PPh_3)] (**1**) gives the unusual metalation product [Ru(η^5-indenyl)(CH_2CN)(HPR_2)(PPh_3)] (**2**), which has been structurally characterized. This reaction clearly demonstrates high Brønsted basicity at the terminal phosphido ligand in **1**. $^{31}P\{^1H\}$ NMR studies show that less acidic N-donor solvents simply disrupt the Ru−P π-bond in **1** to give adducts [Ru(η^5-indenyl)(L)(HPR_2)(PPh_3)] (L = benzonitrile (**6**) or pyridine (**7**)), which are in equilibrium with **1** and free L. The analogous acetonitrile adduct (**4**) was observed by NMR at 240 K during the formation of **2**, but is quickly replaced by **2** at higher temperatures. NMR studies of an alternate route to the metalated complex **2**, starting from the cationic N-bound acetonitrile adduct [Ru(η^5-indenyl)($NCCH_3$)-($HPCy_2$)(PPh_3)][PF_6] (**3a**), along with the demonstrated lability of the benzonitrile and pyridine adducts, suggest that the metalation of acetonitrile by **1** proceeds via an intermolecular C−H addition across the Ru═P double bond, rather than the intramolecular C−H activation of N-bound acetonitrile. This is confirmed by the observation, by $^{31}P\{^1H\}$ NMR, of multiple product isotopomers in the reaction of **1** with a 1:1 mixture of d_3- and d_0-acetonitrile. O-Donor solvents also deprotonated by **1** include water, alcohols, and acetone, which give the complexes [Ru(η^5-indenyl)(X)($HPCy_2$)(PPh_3)], where X = OR (**8**), $CH_2(=O)CH_3$ (**10**).

Introduction

Acetonitrile is an extremely useful solvent in coordination chemistry. Its polarity allows dissolution of the salts of complex ions and other polar transition metal complexes. Its donor ability, via the nitrile N, allows stabilization of low-coordinate species in solution and their subsequent crystallization as nitrile adducts. As a ligand, N-bound acetonitrile is sufficiently labile toward substitution by other donor ligands that it finds widespread use in transition metal precursor complexes.[1] Thus, mechanisms for both stoichiometric and catalytic reactions carried out in acetonitrile frequently invoke this neutral N-donor as a benign placeholder ligand. That being said, there is an appreciable literature concerned with metal-mediated reduction of the acetonitrile C−N triple bond, which typically involves the participation of N-bound or η^2-CN-bound acetonitrile ligands, leading to formation of new C−H, C−O, C−C, and/or N−H bonds.[2,3] Activation of the C−C bond in acetonitrile, via similar intermediate complexes, is also known.[4] Examples of the metalation of acetonitrile[5,6] to give M-CH_2CN complexes are surprisingly rare, although such C−H bond activation is sometimes implicit from product analysis.[7] Complexes resulting from the oxidative addition of acetonitrile include [Ir(PMe_3)$_4$-(CH_2CN)(H)]Cl[8] and [M(dmpe)$_2$(CH_2CN)(H)] (M = Fe, Ru).[9] Dinuclear lanthanide complexes containing μ-κ^2-CH_2CN ligands form via silane elimination when acetonitrile is added to trimethylsilyl precursor complexes.[10] Other apparent examples of the direct metalation of acetonitrile result from the oxidative addition of the C−Cl bond of chloroacetonitrile (e.g., [Pt(PPh_3)$_2$(CH_2CN)(Cl)][11] and [Ni(dippe)(CH_2CN)(Cl)][4]) and subsequent reduction of the metal−chloride bond, or from metathesis of metal halide precursors with "pre-metalated" acetonitrile (e.g., [Ni(η^5-Cp)(CH_2CN)(PPh_3)], prepared using *n*-BuLi/CH_3CN).[12]

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987; p 199.

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(3) See for example:Pittard, K. A.; Cundari, T. R.; Gunnoe, T. B.; Day, C. S.; Petersen, J. L. *Organometallics* **2005**, *24*, 5015. Bianchini, C.; Meli, A.; Moneti, S.; Vizza, F. *Organometallics* **1998**, *17*, 2636. Joshi, A. M.; MacFarlane, K. S.; James, B. R.; Frediana, P. *Chem. Ind. (Dekker)* **1994**, *53*, 497. Chin, C. S.; Lee, B. *Catalysis* **1992**, *14*, 135. Rhodes, L. F.; Venanzi, L. M. *Inorg. Chem.* **1987**, *26*, 2692. Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536.

(4) Atesin, T. A.; Li, T.; Lachaize, S.; Brennessel, W. W.; Garcia, J. J.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 7562.

(5) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic Press: Orlando, 1985; Chapter 2. The pK_a of 24 for acetonitrile was measured in DMSO and converted to a measurement in H_2O. All other pK_a values mentioned in this article were measured in H_2O.

(6) The C−H bond strength in acetonitrile is ~97 kcal/mol. Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1987; pp 9−61.

(7) See for example: (a) Cobalt-mediated H/D exchange from solvent CD_3CN: Fujita, E.; Creutz, C. *Inorg. Chem.* **1994**, *33*, 1729. (b) Formation of novel crotonitrileamido ligands from acetonitrile metalation at yttrium: Duchateau, R.; vanWee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291. (c) α-C−H activation of nitriles: Murahashi, S.; Takaya, H. *Acc. Chem. Res.* **2000**, *33*, 225.

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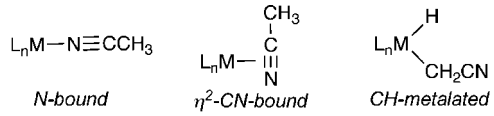
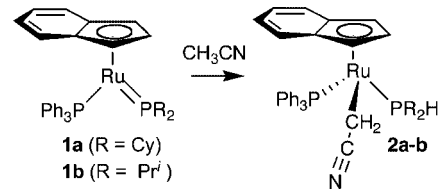


We recently isolated the terminal phosphido complex [Ru(η^5-indenyl)(PR$_2$)(PPh$_3$)] (**1**), in which a novel Ru=PR$_2$ double bond offsets coordinative unsaturation at the five-coordinate Ru center.[13] Although complex **1** is soluble in nonpolar hydrocarbon solvents such as hexanes and benzene, we needed to identify a more polar solvent for mechanistic studies of a range of 2+2-cycloaddition reactions at the Ru−P double bond in **1**.[14] Of the solvents we screened, acetonitrile gave the most surprising result. We report here its reaction with **1** to give the unusual metalated product [Ru(η^5-indenyl)(CH$_2$CN)(HPR$_2$)(PPh$_3$)] (**2**, Scheme 1), an overall 1,2-addition of the acetonitrile C−H bond across the Ru−P double bond in **1**. We place this reaction in the context of the interactions of **1** with other N- and O-donor solvents. The chemistry described here and the clean formation of **2** highlight the potential utility of the terminal phosphido group in metal-mediated chemistry: it is a ligand of variable coordination mode, which also acts as a potent internal base.

Results and Discussion

The addition of excess acetonitrile to dark blue solutions of **1** in d_8-toluene gives an immediate color change to yellow-orange. ^{31}P{^{1}H} NMR spectroscopy indicates disappearance of the downfield peaks corresponding to planar phosphido ligands (276.3 (**1a**), 288.3 (**1b**) ppm) and the appearance of new peaks at 71.4 (**2a**) and 78.4 (**2b**) ppm, which show large $^1J_{PH}$ ~324−330 Hz in the corresponding proton-coupled ^{31}P spectra (Table 1). ^{1}H NMR spectra also confirm the P−H bond in **2**, showing doublets of multiplets at 3.86 (**2a**) and 3.98 (**2b**) ppm with matching $^1J_{PH}$ splittings. ^{1}H peaks due to the diastereotopic methylene protons of the CH$_2$CN ligand are seen at 1.14, 0.80 (**2a**) and 1.05, 0.79 (**2b**) ppm; these multiplets become simple doublets with $^2J_{HH}$ = 2.0 Hz in the corresponding ^{1}H{^{31}P} spectra. These assignments are confirmed by correlation to ^{13}C{^{1}H} peaks for the unique, Ru-bound methylene carbon at −25.6 (**2a**) and −25.9 (**2b**) ppm in the ^{1}H/^{13}C HSQC spectra and to the nitrile carbon peak (133.1 (**2a**), 133.0 (**2b**) ppm) in the ^{1}H/^{13}C HMBC spectra. Infrared spectroscopy also supports the metalated structure of **2**: in addition to ν_{PH} (2332 (**2a**) and 2296 (**2b**) cm^{-1}), we observe ν_{CN} at 2179 (**2a**) and 2181 (**2b**) cm^{-1}. These are lower frequencies than for N-bound acetonitrile in [Ru(η^5-indenyl)(NCCH$_3$)(HPR$_2$)(PPh$_3$)]PF$_6$ (**3**, vide infra, ν_{CN} = 2272 cm^{-1}),[15] although they are considerably higher than those reported for the corresponding alkali metal carbanions,[16] suggesting a less ionic metal−carbon interaction in **2**.[17] Finally, X-ray diffraction analysis of a single crystal of **2a** gives unequivocal evidence for its metalated structure in the solid state (Figure 1).

Scheme 1



The metalation of acetonitrile by **1** was a surprise on several counts. We had anticipated that **1** might react with acetonitrile to form an N-bound adduct (**4**) (Scheme 2),[18] analogous to the deep red, six-coordinate carbonyl adduct [Ru(η^5-indenyl)(PR$_2$)(CO)(PPh$_3$)] (**5**),[19] in which the terminal phosphido ligand persists, but has pyramidal, instead of planar, geometry at phosphorus and has a much longer Ru−P single bond.[20] Analogous N-bound adducts (**6**) result from the addition of benzonitrile to d_8-toluene solutions of **1**. Pyramidal geometry at the phosphido ligands in complexes **6a**,**b** is evident from their upfield ^{31}P chemical shifts and extremely small $^2J_{PP}$ coupling (<5 Hz) to coordinated PPh$_3$ (Table 1).[13,21] Small amounts of **1** remain in equilibrium with adducts **6** in these mixtures, even in the presence of excess benzonitrile.[22] The addition of excess pyridine to d_8-toluene solutions of **1a**,**b** gives similar equilibria, but N-bound adducts **7a**,**b** are observed only at low temperature: at temperatures above 290 K the mixtures decompose to a number of as-yet unidentified products. Despite the fact that pyridine is a stronger donor than benzonitrile,[23] the relative amounts of **1** in these samples are higher than in the benzonitrile samples, and the equilibria shift from **7** toward (**1** + pyridine) as the temperature is raised from 230 K to 290 K. Consistent with this shift is a color change from deep red to blue as the sealed NMR samples are thawed and warmed. Van't Hoff

(12) Davidson, J. G.; Barefield, E. K.; Vanderveer, D. G. *Organometallics* **1985**, *4*, 1178.

(13) Derrah, E. J.; Pantazis, D. A.; McDonald, R.; Rosenberg, L. *Organometallics* **2007**, *26*, 1473.

(14) Derrah, E. J.; Pantazis, D. A.; McDonald, R.; Hall, S. A.; Rosenberg, L., manuscript in preparation.

(15) N-Coordinated nitriles often exhibit a shift of ν_{CN} to higher frequency than that for the free nitrile (ref 2). For free acetonitrile, ν_{CN} = 2254 cm^{-1}: SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, July 25, 2007).

(16) For MCH$_2$CN, where M = Li, Na, K, ν_{CN} = 2049−2051 cm^{-1}. Juchnovski, I. N.; Dimitrova, J. S.; Binev, I. G.; Kaneti, J. *Tetrahedron* **1978**, *34*, 779.

(17) See ref 9 for further discussion of ν_{CN} for M-CH$_2$CN complexes.

(18) Another possible outcome was the 2+2-cycloaddition of the CN triple bond in acetonitrile and the Ru=PR$_2$ bond in **1**. Although previously observed for a bent phosphinidene fragment (M=PR; Hou, Z. M.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158) and for a Schrock carbene complex (M=CR$_2$; Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210), we see no evidence for this reaction.

(19) We reported **5a** previously (ref 13); **5b** was prepared similarly, by sealing an NMR sample of **1b** under an atmosphere of carbon monoxide. For **5b**, ^{31}P{^{1}H} (145.78 MHz, d_8-toluene, δ): 67.7 (d, $^2J_{PP}$ = 9 Hz, *P*Pr$^i_2$), 51.6 (d, *P*Ph$_3$).

(20) (a) This switch in phosphido coordination mode (planar vs pyramidal) is similar to the well-established hemilability of the nitrosyl ligand (linear vs bent), as has been noted previously: Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1986**, *5*, 1612. Similar adduct formation is observed for other "operationally unsaturated", five-coordinate ruthenium complexes: (b) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

(21) (a) Planas, J. G.; Hampel, F.; Gladysz, J. A. *Chem.−Eur. J.* **2005**, *11*, 1402. (b) Given the importance of strong donor ancillary ligands in the P-basic complexes described in (a), it is perhaps not surprising that complex **5**, a comparable 18e$^-$ complex with a π-acidic CO ligand, does not cause isotope scrambling when added to a 1:1 mixture of d_0- and d_3-acetonitrile. (See Experimental Section.)

(22) (a) This equilibrium is evident in ^{31}P{^{1}H} spectra of sealed samples containing **1** and excess benzonitrile (see Experimental Section and Supporting Information). While pure **1a**,**b** in d_8-toluene slowly decompose at room temperature in solution via the orthometalation of a phenyl group on the coordinated triphenylphosphine ligand, to give [Ru(η^5-indenyl)(HPR$_2$)(κ^2-*o*-C$_6$H$_4$PPh$_2$)] (ref 13), the absence of this product in samples of **1** and excess benzonitrile that have stood for 24 h or longer suggests that *reversible* formation of **6** is fast relative to the orthometalation reaction (i.e., lifetimes of **1** in the equilibrium mixtures are sufficiently short to preclude this slow thermal decomposition). (b) We see no evidence for the analogous, reversible dissociation of CO from complex **5** in solution. (See Experimental Section.)

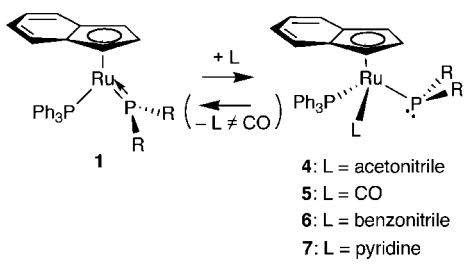
(23) A useful measure of "donicity" (Lewis basicity) of the solvents studied is their donor number, "DN". (a) Gutmann, V.; Schmid, R. *Coord. Chem. Rev.* **1974**, *12*, 263. (b) For pyridine, acetonitrile, and benzonitrile, DN = 33.1, 14.1, and 11.9, respectively.

Table 1. $^{31}P\{^1H\}$ NMR Data for New Compounds: δ (ppm) (multiplicity, $^2J_{PP}$ or $\omega_{1/2}$ (Hz))

complex		PR_2/HPR_2	PPh_3	$^1J_{PH}$[a]
[Ru(η^5-indenyl)(CH_2CN)($HPCy_2$)(PPh_3)]	**2a**[b]	72.4 (d, 38)	58.8 (d)	330
[Ru(η^5-indenyl)(CH_2CN)($HPPr^i_2$)(PPh_3)]	**2b**[b]	78.3 (d, 33)	58.9 (d)	324
[Ru(η^5-indenyl)($NCCH_3$)($HPCy_2$)(PPh_3)]PF_6	**3a**[c]	57.1 (d, 36)	52.8 (d)	344
[Ru(η^5-indenyl)($NCCH_3$)($HPPr^i_2$)(PPh_3)]PF_6	**3b**[c]	67.0 (d, 36)	52.2 (d)	340
[Ru(η^5-indenyl)(PCy_2)($NCCH_3$)(PPh_3)]	**4a**[d,e]	65.2 (s)	54.4 (s)	
[Ru(η^5-indenyl)(PPr^i_2)($NCCH_3$)(PPh_3)]	**4b**[d,e]	74.0 (s)	53.8 (s)	
[Ru(η^5-indenyl)(PCy_2)(py)(PPh_3)]	**6a**[d,e]	82.9 (br s, 29)	51.0 (br s, 20)	
[Ru(η^5-indenyl)(PPr^i_2)(py)(PPh_3)]	**6b**[d,e]	95.8 (br s, 18)	48.2 (br s, 19)	
[Ru(η^5-indenyl)(PCy_2)(NCPh)(PPh_3)]	**7a**[d,f]	68.9 (s)	54.1 (s)	
[Ru(η^5-indenyl)(PPr^i_2)(NCPh)(PPh_3)]	**7b**[d,f]	79.0 (s)	53.6 (s)	
[Ru(η^5-indenyl)(OH)($HPCy_2$)(PPh_3)]	**8a-H**[d]	66.8 (d, 46)	55.0 (d)	343
[Ru(η^5-indenyl)(OH)($HPPr^i_2$)(PPh_3)]	**8b-H**[d]	75.9 (d, 44)	54.8 (d)	325
[Ru(η^5-indenyl)(OMe)(PPh_3)($HPCy_2$)]	**8a-Me**[d,f]	65.3 (d, 48)	55.6 (d)	340
[Ru(η^5-indenyl)(OMe)(PPh_3)($HPPr^i_2$)]	**8b-Me**[d,f]	75.5 (d, 48)	53.8 (d)	348
[Ru(η^5-indenyl)(OBu^t)($HPCy_2$)(PPh_3)]	**8a-Bu^t**[d]	68.1 (d, 44)	55.0 (d)	341
[Ru(η^5-indenyl)(OBu^t)($HPPr^i_2$)(PPh_3)]	**8b-Bu^t**[d]	77.2 (d, 44)	54.7 (d)	315
[Ru(η^5-indenyl)($CH_2C(O)CH_3$)($HPCy_2$)(PPh_3)]	**10a**[d,g]	67.9 (d, 42)	54.7 (d)	329
[Ru(η^5-indenyl)($CH_2C(O)CH_3$)($HPPr^i_2$)(PPh_3)]	**10b**[d,e]	77.2 (d, 44)	54.1 (d)	338

[a] Measured in Hz from corresponding ^{31}P spectrum or (**3a**,**b**) ^1H NMR spectrum. [b] 202.4 MHz, samples in d_6-benzene. [c] 202.4 MHz, samples in d_1-chloroform; for both **3a**,**b**, $\delta PF_6 = -143.6$ ppm, $^1J_{PF} = 713$ Hz. [d] 145.8 MHz, samples in d_8-toluene. [e] Recorded at 240 K. [f] Recorded at 250 K. [g] Recorded at 260 K.

Scheme 2



analysis of the temperature dependence of K_{eq} for (**1** + pyridine) = **7** gave the following thermodynamic parameters (listed for **a**, **b**): $\Delta H°$ (kcal/mol) = −8.4, −7.6; $\Delta S°$ (cal/K/mol) = −14, −10; $\Delta G°$(240 K) (kcal/mol) = −4.8, −5.0. These data point to entropic control of the equilibrium between **1** and **7**: loss of entropy causes the equilibrium to shift away from adduct formation at higher temperatures, although adduct **7** is enthalpically favored over (**1** + free pyridine).[24] We presume the decreased stability of **7**, relative to **6**, stems from the considerable crowding at Ru in these N-bound adducts.

When the reaction of acetonitrile with **1** is monitored at low temperature by $^{31}P\{^1H\}$ NMR, we do observe transient signals due to the N-bound acetonitrile adducts, **4** (Table 1). This raises the question of whether **4** is an intermediate in the formation of the metalation product, **2**. Intramolecular proton abstraction by the phosphido ligand from N-bound acetonitrile seems unlikely, since the linear, N-bound nitrile functionality places the acetonitrile C−H bonds quite far from the Ru−P bond in **4**. Also, the equilibria we observe between **1** and its benzonitrile (**6**) and pyridine (**7**) adducts suggest that the acetonitrile ligand in **4** is probably quite labile, so our observation of **4** does not preclude intermolecular activation by **1** of the C−H bond in free acetonitrile. To gain further insight into the possible involvement of **4** in the formation of **2**, we monitored by $^{31}P\{^1H\}$ NMR the reaction of $KOBu^t$ with the cationic, N-bound acetonitrile complex **3a** (Scheme 3, an alternate synthetic route

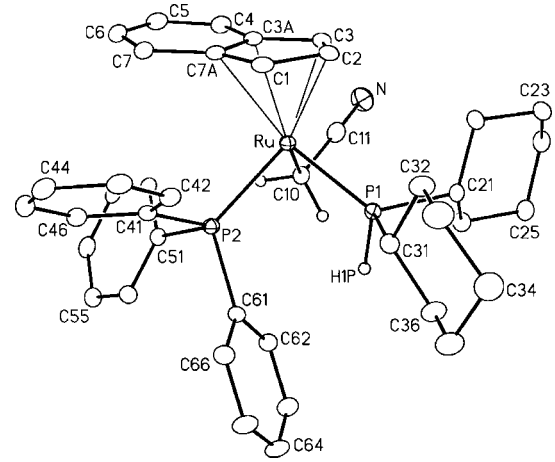


Figure 1. Molecular structure of **2a**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and C10 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Selected interatomic distances (Å) and bond angles (deg) (C* denotes the centroid of the plane defined by C(7A)−C(1)−C(2)−C(3)−C(3A)): Ru−P(1) = 2.2512(7), Ru−P(2) = 2.2969(7), Ru−C10 = 2.178(3), Ru−C* = 1.925, Δ = 0.115, C(10)−C(11) = 1.452(4), C(11)−N = 1.141(4); P(1)−Ru−P(2) = 91.57(2), P(1)−Ru−C(10) = 86.40(7), P(2)−Ru−C(10) = 90.05(7), P(1)−Ru−C* = 127.8, P(2)−Ru−C* = 125.9, C(10)−Ru−C* = 123.3, Ru−C(10)−C(11) = 112.81(19), C(10)−C(11)−N = 179.2(3). Indenyl slip distortion: $\Delta = d$[Ru−C(7A),C(3A)] − d[Ru−C(1),C(3)] = 0.115 Å.

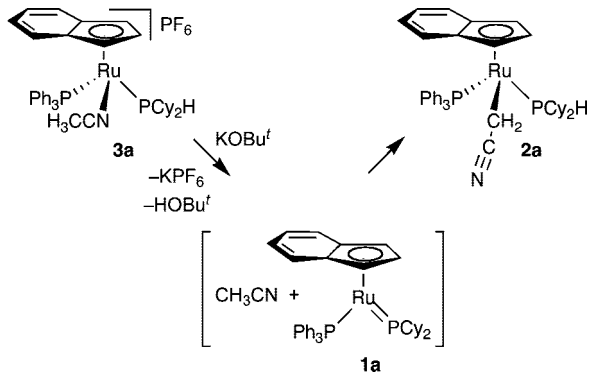
to **2a**). Initial spectra indicate the rapid, complete consumption of **3a**, with formation of both **1a** (minor) and **2a** (major), but there is no sign of **4a**.[25] This is consistent with facile dissociation of acetonitrile early in the reaction, followed by formation of **1a** and its intermolecular reaction with free acetonitrile, but does not rule out either (i) rapid consumption of transient **4a**, whose concentration would be low in the absence of excess acetonitrile in the mixture, or (ii) a competitive pathway in which the acetonitrile, rather than the secondary phosphine in **3a**, is

(24) The exchange of pyridine between the bulk mixture and **7** was sufficiently slow on the NMR time scale to allow line-shape analysis of $^{31}P\{^1H\}$ NMR spectra recorded at different temperatures and calculation of activation parameters for this exchange (conversion of **1a**,**b** to **7a**,**b**, respectively). Eyring data: $\Delta H^‡$(kcal/mol) = 8.8, 6.7; $\Delta S^‡$(cal/K/mol) = −16,−23; $\Delta G^‡$(240 K) (kcal/mol) = 13, 13. Arrhenius data: E_a(kcal/mol) = 9.3, 7.2. See Supporting Information for full details.

(25) The identity of these products early in the reaction is certain; however, low solubility of **3a** and $KOBu^t$ in d_8-toluene and the production of gelatinous Bu^tOH and solid KPF_6 in the NMR sample render this experiment a bit messy and difficult to monitor to completion.

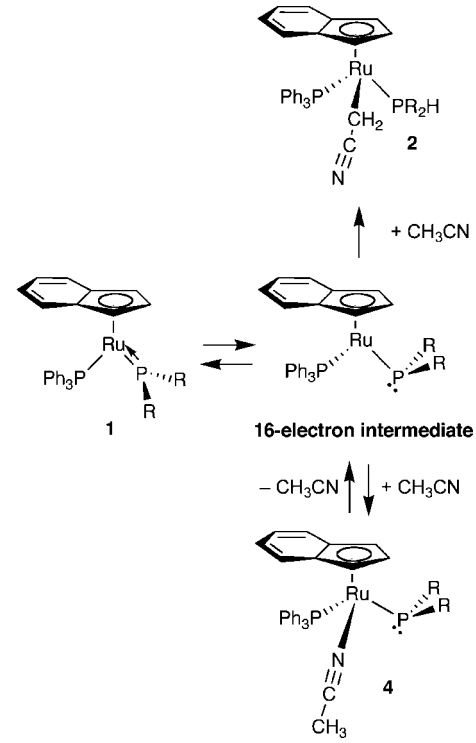
deprotonated by KOBu^t. Initial $^{31}P\{^1H\}$ NMR spectra of the analogous reaction using the CD_3CN analogue of **3a** show mostly unreacted d_3-**3a**, no **4a**, a small amount of **1a**, and just a tiny amount of **2a**.[26] While this experiment points qualitatively to a deuterium isotope effect on the rate of metalation of acetonitrile, again it does not preclude the intermediacy of **4a** in the reaction. More compelling evidence for an intermolecular pathway from **1** to **2** comes from the addition of a 1:1 mixture of d_3- and d_0-acetonitrile to **1a**,**b**. The relative amount of deuterium incorporated into the P−H position in the products **2a**,**b** in these reactions indicates kinetic isotope effects (2.0 and 3.2, respectively) consistent with the importance of the C−H bond breaking in the transition state of the reaction. $^{31}P\{^1H\}$ NMR spectra of these product mixtures clearly indicate the presence of at least four isotopomers (attributable to $d_{0,1,2,3}$-**2**), whereas only two (pure d_3- and d_0-**2**) would be expected for the intramolecular metalation of acetonitrile via adduct **4**.

Scheme 3



The formation of complex **2** demonstrates much higher Brønsted basicity at the phosphido ligand in **1** than we expected. Although P-nucleophilicity/basicity is an established feature of terminal phosphido complexes of Ru and other late metals,[21,27] and we previously observed protonation of the planar PR_2 group in **1a** by HCl and NH_4Cl (and its methylation, by MeI);[13] nevertheless, the observed deprotonation of acetonitrile suggests that pK_a values for conjugate acids of **1a**,**b** are extraordinarily high, given the participation of the lone pair on this phosphido ligand in a π-bond with ruthenium. They approach those reported for the conjugate acids of pyramidal phosphido ruthenium complexes [Ru(η^5-Cp)(PR_2)(PR'_3)$_2$] (estimated pK_a (H_2O or THF) ~20−25), in which PR_3' are highly Lewis basic trialkylphosphines.[21] It is possible, in these reactions of **1**, that a 16-electron intermediate with a single Ru−P bond and pyramidal geometry at the phosphido P is key to the high basicity we observe, as well as providing the open coordination site that leads to adduct formation at Ru (Scheme 4). Preliminary DFT calculations,[28] examining the trajectory of formation of **5a** from **1a**, have uncovered such an intermediate, at approximately 6.7 kcal/mol higher energy than **1a**, with the sum of angles at PCy2 of 340.6° and a Ru−PCy_2 distance of 2.211 Å, relative to 2.166 Å calculated for **1a**.[13] Hypothetical pathways

Scheme 4



to this intermediate are currently under computational investigation. If kinetically accessible, it provides a convincing picture for a competition between reversible binding of acetonitrile and its intermolecular activation by **1** (Scheme 4), in which the outcome is dictated by high stability of the C−H metalated product, **2**.

In the context of the high P-basicity implied by the formation of **2**, it is not surprising that protic O-donor solvents H_2O and MeOH (pK_a = 15.74 and 15.5, respectively[5]) are also quantitatively deprotonated by **1** (Scheme 5), giving the corresponding hydroxide (**8-H**) and methoxide (**8-Me**) complexes (Table 1). (The latter rapidly decarbonylates, even at low temperature, to give the hydride complex **9**.[29]) Addition of excess Bu^{t}OH (pK_a = 19.2[5]) to **1a**,**b** gives only partial conversion (15% (**a**), 36% (**b**)) to the corresponding *tert*-butoxide complex **8-Bu^t** (Scheme 5, Table 1), along with several other unidentified products, as determined by $^{31}P\{^1H\}$ NMR. This is surprising, since the reaction of **1** with acetonitrile (a weaker acid) goes to completion, but it can be rationalized by the size of the *tert*-butoxy group, which presumably disfavors formation of the Ru−O bond at this crowded ruthenium center. We see no evidence in these reactions for the formation of O-bound adducts of the neutral ROH. This may reflect the relatively high rate of proton abstraction from these reagents by **1**, but it is also consistent with our observation that diethyl ether and THF, which have comparable O-donor ability[30] to water and methanol (and are presumably much weaker C−H acids), do not react with **1**, as long as they are rigorously dried. Acetone also has comparable O-donor ability to water,[30] but is a relatively strong C−H acid (pK_a = 19):[5] it reacts with **1** to give ~80% of the C−H metalated product **10**, identified by ^{31}P NMR at low

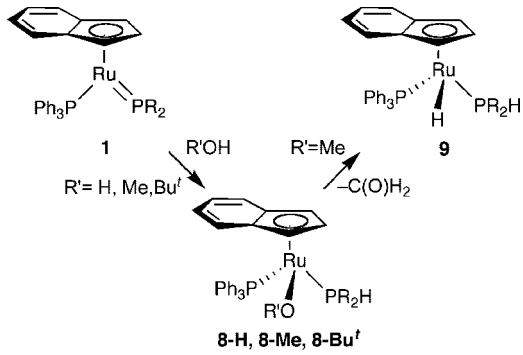
(26) When the reaction of d_3-**3a** with KOBu^t is carried out on a synthetic scale and allowed to go to completion, the solid **2a** isolated is a mixture of d_3- and d_2-isotopomers, the latter containing P−H instead of P−D bonds (see Experimental Section and Supporting Information). This may indicate the non-innocence of Bu^{t}OH initially formed or the direct abstraction of deuterium by KOBu^t from d_3-acetonitrile.

(27) See Chan, V. S.; Stewart, I. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 2786 and Scriban, C.; Glueck, D. S. *J. Am. Chem. Soc.* **2006**, *128*, 2788 and references therein.

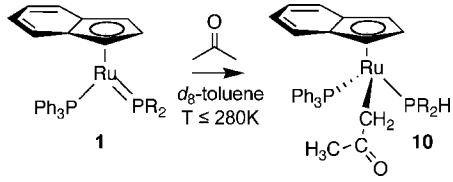
(28) Pantazis, D. A., personal communication.

(29) Complex **9a** was prepared previously by the addition of methanolic sodium methoxide to [Ru(η^5-indenyl)Cl(HPR_2)(PPh_3)] (ref 32). Complex **9b** was identified spectroscopically; $^{31}P\{^1H\}$ (145.78 MHz, d_8-toluene, δ): 72.2 (d, $^2J_{PP}$ = 28 Hz, H*P*Pr$^i_2$), 70.0 (d, *P*Ph$_3$).

Scheme 5



Scheme 6



temperature (Scheme 6, Table 1).[31] At temperatures above 280 K, mixtures of **1** and **10** decompose to a number of unidentified products.

Conclusions

The above reactions of a range of N- and O-donor solvents demonstrate a delicate balance between Lewis acidity at ruthenium and Brønsted basicity at the phosphido phosphorus in **1**. This is highlighted by the fact that we are able to observe the N-bound acetonitrile adduct **4** at low temperatures *and* "trap" the methylenenitrile anion in **2**. We are currently investigating reactions of **2** that might allow further transformation of this functional anion via the Ru−C bond. Future work will focus on more generally exploiting the cooperation between the inner and outer coordination sphere at ruthenium in **1**, which is provided by the variable coordination mode and basicity of the terminal phosphido ligand in this system.

Experimental Section

General Details. Unless otherwise noted, all reactions and manipulations were performed under nitrogen in an MBraun Unilab 1200/780 glovebox or using conventional Schlenk techniques. All solvents were sparged with nitrogen for 25 min and dried using an MBraun solvent purification system (SPS) except: benzene was freeze−pump−thaw degassed and vacuum transferred from sodium/benzophenone prior to use; acetone was dried over K_2CO_3 prior to distillation under nitrogen; pyridine was dried over $MgSO_4$ prior to distillation under nitrogen; benzonitrile was predried with K_2CO_3, then fractionally distilled from P_2O_5 under dynamic vacuum; Bu^{t}OH was dried over Na and a small amount of benzene was added prior to fractional distillation under nitrogen to remove remaining water as a tertiary azeotrope; H_2O was freeze−pump−thaw degassed; and Et_2O was dried over CaH_2 prior to distillation under nitrogen. Deuterated solvents were purchased from Canadian Isotope Laboratories (CIL), freeze−pump−thaw degassed, and vacuum transferred from sodium/benzophenone (d_6-benzene, d_8-toluene) or calcium hydride (d-chloroform, d_3-acetonitrile) before use. [RuCl(η^5-indenyl)(HPCy$_2$)(PPh$_3$)],[32] [RuCl(η^5-indenyl)(HPPr$^i_2$)(PPh$_3$)],[13] [Ru(η^5-indenyl)(PCy$_2$)(PPh$_3$)] (**1a**),[13] [Ru(η^5-indenyl)(PPr$^i_2$)(PPh$_3$)$_2$] (**1b**),[13] and [Ru(η^5-indenyl)(PCy$_2$)(CO)(PPh$_3$)] (**5a**)[13] were prepared as previously reported. NMR spectra were recorded on a Bruker AVANCE 500 operating at 500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C, and 202.46 MHz for ^{31}P, or on a Bruker AVANCE 360 operating at 360.13 MHz for ^{1}H, 55.28 MHz for ^{2}H, and 145.78 MHz for ^{31}P. Chemical shifts are reported in ppm at ambient temperature unless otherwise noted. ^{1}H chemical shifts are referenced against residual protonated solvent peaks at 7.16 ppm (C_6D_5H), 2.09 ppm ($PhCD_2H$), and 7.24 ppm ($CHCl_3$). ^{2}H chemical shifts are referenced against trace C_6H_5D in benzene. ^{13}C chemical shifts are referenced against d_6-benzene at 128.4 ppm and d-chloroform at 77.5 ppm. All ^{1}H, ^{2}H, and ^{13}C chemical shifts are reported relative to tetramethylsilane, and ^{31}P chemical shifts are reported relative to 85% H_3PO_4(aq). Microanalysis was performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. IR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrophotometer using KBr pellets under a nitrogen atmosphere. Mass spectrometry was carried out by Dr. David McGillivray at the Department of Chemistry, University of Victoria.

[Ru(η^5-indenyl)(CH$_2$CN)(HPCy$_2$)(PPh$_3$)] (2a). To a Schlenk flask containing a blue solution of [Ru(η^5-indenyl)(PCy$_2$)(PPh$_3$)$_2$] (100 mg, 0.15 mmol) in toluene (5 mL) was added acetonitrile (0.8 mL, 0.6 g, 20 mmol). The resulting orange solution was allowed to stir for 1.5 h before the solvent was evaporated under vacuum to give a dark orange oil. Recrystallization from toluene (2 mL) and pentane (20 mL) at −30 °C gave a dark brown crystalline solid (**2a**, 56 mg, 0.074 mmol, 53% yield) along with two unidentified complexes as minor impurities (<5%). The sample was recrystallized a second time from toluene (1−2 mL) by the slow vapor diffusion of pentane (10 mL) to give **2a** (44 mg, 0.061 mmol, 79% yield) in >99% purity. IR (KBr, cm^{-1}): 2332 (w, ν_{P-H}), 2179 (s, ν_{CN}). FAB-MS (+LSIMS matrix mNBA; *m/z* (relative intensity): 717.3 (8%) [M$^+$], 677.3 (83%) [M$^+$ − CH$_2$CN], 479.1 (100%) [M$^+$ − CH$_2$CN − HPCy$_2$]. HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{41}H_{47}NP_2Ru$ 717.2227; found 717.2227 ± 0.0020 (average of 3 trials). Anal. Calcd for $C_{41}H_{47}NP_2Ru$: C, 68.70; H, 6.61. Found: C, 67.52; H, 6.47 (see Supporting Information for ^{1}H and ^{31}P{^{1}H} NMR). Dec pt: 196−198 °C.

[Ru(η^5-indenyl)(CH$_2$CN)(HPPr$^i_2$)(PPh$_3$)] (2b). To a Schlenk flask containing a blue solution of [Ru(η^5-indenyl)(PPr$^i_2$)(PPh$_3$)$_2$] (100 mg, 0.17 mmol) in toluene (5 mL) was added acetonitrile (0.8 mL, 0.6 g, 20 mmol). The resulting orange solution was allowed to stir for 1.5 h before the solvent was evaporated under vacuum to give a dark yellow oil. Pentane (10 mL) was added, and the mixture was allowed to stir for 3 h. The resulting yellow suspension was filtered and washed with pentane (3 × 10 mL) to give [Ru(η^5-indenyl)(CH$_2$CN)(HPPr$^i_2$)(PPh$_3$)$_2$] (**2b**) (76 mg, 0.12 mmol, 71% yield) along with two unidentified complexes as minor impurities (<5%). Crude **2b** (61 mg, 0.10 mmol) was recrystallized by the vapor diffusion of pentane (10 mL) into a toluene solution (1 mL) to give an orange crystalline solid (30 mg, 0.05 mmol, 49% yield). IR (KBr, cm^{-1}): 2296 (m, ν_{PH}), 2181 (s, ν_{CN}). FAB-MS (+LSIMS matrix mNBA; *m/z* (relative intensity): 637.2 (8%) [M$^+$], 597.2 (70%) [M$^+$ − CH$_2$CN], 479.1 (100%) [M$^+$ − CH$_2$CN − HPPr$^i_2$]. HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{35}H_{39}NP_2Ru$ 637.1601; found 637.1591 ± 0.0008 (average of 3 trials). Anal. Calcd for $C_{35}H_{39}NP_2Ru$: C, 66.02; H, 6.17. Found: C, 65.88; H, 6.17. Dec pt: 168−169 °C.

(30) O-Donor strengths vary as DN = 20 (THF) > 19.2 (Et_2O) > 19.0 (MeOH) > 18.0 (water, although this is much higher, 33, for bulk water) >17 (acetone). In ref 23, the authors note that, although overall trends in DN for any given heteroatom donor type are valid, comparisons between different heteroatom donors are not reliable.

(31) The C−H metalation of acetone at ruthenium has been reported for: (a) [RuH (naphthyl)(dmpe)$_2$], with loss of naphthalene (ref 9); (b) [Ru(η^5-Cp*)(OH)(PMe$_3$)$_2$], with loss of H_2O: Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

(32) Derrah, E. J.; Marlinga, J. C.; Mitra, D.; Friesen, D. M.; Hall, S. A.; McDonald, R.; Rosenberg, L. *Organometallics* **2005**, *24*, 5817.

[Ru(η^5-indenyl)(NCCH$_3$)(HPCy$_2$)(PPh$_3$)][PF$_6$] (3a). To a Schlenk flask containing an orange suspension of [Ru(η^5-indenyl)Cl(HPCy$_2$)(PPh$_3$)] (215 mg, 0.30 mmol) and [NH$_4$][PF$_6$] (148 mg, 0.90 mmol, 3 equiv) in methanol (5 mL) was added acetonitrile (2.0 mL, 1.6 g, 38 mmol). No immediate reaction was observed, but after the mixture had stirred for 2 days a yellow precipitate formed, which was isolated by filtration, then redissolved in CH_2Cl_2 (5 mL). The resulting yellow solution was filtered to remove unreacted [NH$_4$][PF$_6$], and the volume was reduced (50%) under vacuum. Hexanes (40 mL) was added, which gave **3a** (218 mg, 0.25 mmol, 84% yield) as an orange crystalline solid. IR (KBr, cm^{-1}): 2334 (w, ν_{PH}), 2272 (w, ν_{CN}). FAB-MS (+LSIMS matrix mNBA; *m/z* (relative intensity): 718.2 (8%) [M$^+$], 677.0 (100%) [M$^+$ − CH$_3$CN], 478.9 (33%) [M$^+$ − CH$_3$CN − HPCy$_2$]. HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{41}H_{48}NP_2Ru$ 718.2306; found 718.2308 ± 0.0012 (average of 3 trials). Anal. Calcd for $C_{41}H_{48}F_6P_3Ru \cdot 0.17CH_2Cl_2$: C, 55.56; H, 5.49. Found: C, 55.31; H, 5.39 (see Supporting Information for ^{1}H NMR). Dec pt: 144−146 °C.

Alternate Preparation of 2a via 3a. To a Schlenk flask containing a yellow suspension of [Ru(η^5-indenyl)(NCCH$_3$)(HPCy$_2$)(PPh$_3$)][PF$_6$] (**3a**) (52 mg, 0.040 mmol) in toluene (5 mL) was added KO^{t}Bu (8 mg, 0.072 mmol, 1.2 equiv). The resulting green solution was stirred for 24 h, during which time it turned black-yellow. After 5 days the solution turned yellow, at which point the solvent was removed under vacuum. The resulting yellow oil was dissolved in a minimal amount of hexanes (5 mL), and a yellow precipitate formed after 24 h. A yellow powder (approximately 10 mg) was isolated by filtration, dried under vacuum, and confirmed to be **2a** by NMR spectroscopy. This reaction was repeated using d_3-**3a** (see below), giving a similar yield of a yellow powder whose ^{1}H and ^{2}H NMR spectra are consistent with a mixture of isotopomers of **2a**.[26]

[Ru(η^5-indenyl)(NCCD$_3$)(HPCy$_2$)(PPh$_3$)][PF$_6$] (d_3-3a). This complex was prepared as described above for **3a**, using [Ru(η^5-indenyl)Cl(HPCy$_2$)(PPh$_3$)] (315 mg, 0.44 mmol) and [NH$_4$][PF$_6$] (231 mg, 1.42 mmol, 3.2 equiv) in methanol (10 mL), and d_3-acetonitrile (1.0 mL, 0.8 g, 20 mmol). The product, ***d*$_3$-3a**, was isolated as a yellow powder (312 mg, 0.36 mmol, 82% yield), and its identity was confirmed by ^{1}H and ^{31}P{^{1}H} NMR.

[Ru(η^5-indenyl)(NCCH$_3$)(HPPr$^i_2$)(PPh$_3$)][PF$_6$] (3b). To a Schlenk flask containing an orange solution of [Ru(η^5-indenyl)Cl(HPPr$^i_2$)(PPh$_3$)] (205 mg, 0.32 mmol) and [NH$_4$][PF$_6$] (158 mg, 0.97 mmol, 3 equiv) in MeOH (5 mL) was added acetonitrile (2 mL, 1.6 g, 38 mmol). No immediate reaction was observed, but after the mixture had stirred for 2 days a yellow solution formed. The solvent was removed under vacuum, and the resulting yellow oil was redissolved in CH_2Cl_2 (5 mL), which was filtered to remove unreacted [NH$_4$][PF$_6$]. The volume was reduced (50%) under vacuum, and hexanes (20 mL) was added to give 182 mg (0.23 mmol, 72% yield) of **3b** as an orange crystalline solid. A portion (100 mg, 0.13 mmol) was recrystallized a second time from CH_2Cl_2 (2 mL) and hexanes (20 mL) to give analytically pure **3b** (68 mg, 0.086 mmol, 68% yield). IR (KBr, cm^{-1}): 2343 (w, P−H), 2272 (w, CN); FAB-MS (+LSIMS matrix mNBA; *m/z* (relative intensity): 638.2 (8%) [M$^+$], 597.2 (100%) [M$^+$ − CH$_3$CN], 479.1 (65%) [M$^+$ − CH$_3$CN − HPPr$^i_2$]. HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{35}H_{40}NP_2Ru$ 638.1680; found 638.1698 ± 0.0008 (average of 3 trials). Anal. Calcd for $C_{35}H_{40}F_6NP_3Ru \cdot 0.20CH_2Cl_2$ (see Supporting Information for ^{1}H NMR): C, 52.87; H, 5.09. Found: C, 53.23; H, 5.30. Mp: 160−162 °C.

NMR-Scale Experiments Using 1a,b.[33] In the glovebox solid **1** (**a**: 15 mg, 0.022 mmol; **b**: 15 mg, 0.025 mmol) was placed in a sealable NMR tube with d_8-toluene (0.6 mL). In some cases, internal standard hexamethylbenzene (^{1}H) or triphenylphosphine oxide (^{31}P) was also added. The tube was then capped with a Teflon needle valve adaptor, removed from the glovebox, and connected to a Schlenk line. Each sample was degassed using three freeze−pump−thaw cycles, then frozen in N_2(l). Approximately 0.1 mL of the appropriate reagent (1−5 mmol) was transferred under vacuum (acetonitrile, Bu^{t}OH, methanol, ether, THF, acetone) or delivered by syringe (1:1 acetonitrile/d_3-acetonitrile, pyridine, benzonitrile, H_2O), and the tube was flame-sealed. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer. For reactions monitored at low temperature, the solutions were thawed sufficiently to allow mixing and kept cold in an acetone/dry ice bath before being placed in the precooled spectrometer.

(A) Addition of Acetonitrile Monitored at Room Temperature. The mixed reagents gave a dark yellow-orange solution, indicative of the formation of [Ru(η^5-indenyl)(CH$_2$CN)(HPR$_2$)(PPh$_3$)] (**2a**,**b**), prior to being placed in the NMR spectrometer.

For **1a**: ^{31}P{^{1}H} NMR shows **2a** as the major product (93%), along with six or seven minor, unidentified products (7%).

For **1b**: ^{31}P{^{1}H} NMR shows **2b** as the major product (93%), along with five or six minor, unidentified products (7%).

(B) Addition of Acetonitrile Monitored at Low Temperatures. The mixed reagents gave a dark red solution, prior to being placed in the NMR spectrometer, which was precooled to 240 K. When the sample was removed from the spectrometer at room temperature, the solution was dark yellow-orange.

For **1a**: ^{31}P{^{1}H} NMR spectrum at 240 K shows **2a** as the major product (∼45%), along with unreacted **1a** (∼33%), and peaks consistent with the minor product [Ru(η^5-indenyl)(NCCH$_3$)(PCy$_2$)(PPh$_3$)] (**4a**, ∼22%) (Table 1).

For **1b**: ^{31}P{^{1}H} NMR spectrum at 240 K shows **2b** as the major product (∼50%), along with unreacted **1b** (∼18%), and peaks consistent with the minor product [Ru(η^5-indenyl)(NCCH$_3$)(PPr$^i_2$)(PPh$_3$)] (**4b**, ∼32%) (Table 1).

For both samples, ^{31}P{^{1}H} NMR spectra above 240 K showed rapid conversion of mixtures of **1** and **4** to the metalated product **2**.

(C) Addition of 1:1 Acetonitrile/d_3-Acetonitrile at Room Temperature. Two samples were prepared: one in d_8-toluene and one in d_0-toluene for analysis by ^{2}H NMR. In both cases, the mixed reagents gave a dark yellow-orange solution, indicative of the formation of [Ru(η^5-indenyl)(CH$_2$CN)(HPR$_2$)(PPh$_3$)] (**2a**,**b**) and/or its deuterated derivative(s), prior to being placed in the NMR spectrometer. The ^{1}H, ^{2}H{^{1}H}, and ^{31}P{^{1}H} NMR spectra confirmed that a mixture of deuterated and nondeuterated **2a**,**b** had formed. The ^{1}H NMR spectra were used to determine k_H/k_D (**2a**, 2.0; **2b**, 3.2) by comparing the ratio between the P−H (**2a**, 3.86 ppm; **2b**, 3.98 ppm) and the indenyl H2 (5.56, 5.45 ppm) peaks.

(D) Addition of Pyridine Monitored at Low Temperatures. Hexamethylbenzene (**a**, 35.1 mg, 0.22 mmol; **b**, 34.8 mg, 0.21 mmol) and triphenylphosphine oxide (**a**, 6.4 mg, 0.023 mmol; **b**, 6.7 mg, 0.024 mmol) were added to the sealable NMR tube as ^{1}H and ^{31}P NMR standards, respectively. Prior to the addition of pyridine the samples were thoroughly mixed by sonication to ensure all species dissolved. For both **1a**,**b**, the flame-sealed sample was dark red when removed from the acetone/dry ice bath but quickly (∼15 s) turned blue as it was placed in the NMR spectrometer, which was precooled to 210 K (**a**) or 230 K (**b**). The temperature was immediately lowered to 190 K, at which only peaks due to the coordination products [Ru(η^5-indenyl)(pyridine)(PR$_2$)(PPh$_3$)] (**6a**,**b**) were observed by ^{31}P{^{1}H} NMR. As the temperature was increased in 10 K intervals, these peaks decreased in intensity, while those due to the phosphido complexes (**1a**,**b**) increased in intensity, until the temperature was raised to 290 K, at which point the samples decomposed to 10−15 unidentified products. The resulting data were used to calculate K_{eq} at 230−260 K (see Supporting Information).

Table 2. Crystallographic Experimental Details for 2a

formula	$C_{41}H_{47}NP_2Ru$
fw	716.81
cryst dimens (mm)	0.32 × 0.17 × 0.14
cryst syst; space group	orthorhombic; $P2_12_12_1$ (No. 19)
unit cell params	a (Å) 12.3804(9)
	b (Å) 15.0022(11)
	c (Å) 18.9812(13)
	V (Å^3) 3525.4(4)
	Z 4
ρ_{calcd} (g cm^{-3})	1.351
μ (mm^{-1})	0.565
data collection 2θ limit (deg)	54.88
total no. of data collected	30 397 ($-16 \le h \le 15$, $-19 \le k \le 19$, $-24 \le l \le 24$)
no. of indep reflns	8047 ($R_{int} = 0.0443$)
no. of obsd reflns [$I \ge 2\sigma(I)$]	7183
range of transmn factors	0.9251−0.8399
no. of data/restraints/params	8047/0/410
Flack absolute struct param[a]	−0.03 (2)
goodness-of-fit (S) [all data][b]	1.053
R_1 [$I \ge 2\sigma(I)$][b]	0.0301
wR_2 [all data][b]	0.0675
largest diff peak and hole (e Å^{-3})	0.560 and −0.200

[a] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148. [b] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0350P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$); $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

For **1a**: $^{31}P\{^1H\}$ NMR spectrum at 240 K shows 68% **1a** and 32% **6a**.

For **1b**: $^{31}P\{^1H\}$ NMR spectrum at 240 K shows 48% **1b** and 52% **6b**.

(E) Addition of Benzonitrile Monitored at Low Temperatures. Hexamethylbenzene (**a**, 37.4 mg, 0.23 mmol; **b**, 34.0 mg, 0.21 mmol) and triphenylphosphine oxide (**a**, 11.6 mg, 0.042 mmol; **b**, 6.6 mg, 0.024 mmol) were used as internal ^1H and ^{31}P NMR standards, respectively. Prior to the addition of benzonitrile the samples were thoroughly mixed by sonication to ensure all species dissolved. The flame-sealed samples were red when removed from the acetone/dry ice bath but rapidly turned burgundy while being transferred to the spectrometer, which was precooled to 230 K. For both samples at 230 K, peaks due to the benzonitrile adducts [Ru(η^5-indenyl)(PR_2)(NCPh)(PPh_3)] (**7a**,**b**) dominated the $^{31}P\{^1H\}$ NMR spectra, but as the temperature was increased in 10 K intervals to room temperature, small peaks due to the phosphido complex (**1a**,**b**) appeared. No decomposition was observed at room temperature. The changes in relative intensities of **1a**,**b** and **6a**,**b** over this temperature range were not sufficiently large to calculate reliably K_{eq} for the adduct formation.

For **1a**: $^{31}P\{^1H\}$ NMR at 250 K shows 60% **7a**, 16% **1a**, and 24% [Ru(η^5-indenyl)(NH_2CH_2Ph)($HPCy_2$)(PPh_3)].[34]

For **1b**: $^{31}P\{^1H\}$ NMR at 250 K shows 68% **7b**, 18% **1b**, and 14% [Ru(η^5-indenyl)(NH_2CH_2Ph)($HPCy_2$)(PPh_3)].[34]

(F) Addition of Water Monitored at Room Temperature. For both samples, the mixed reagents gave a dark red solution.

For **1a**: $^{31}P\{^1H\}$ NMR shows peaks due to a major product (93%), assigned as [Ru(η^5-indenyl)(OH)($HPCy_2$)(PPh_3)] (**8a-H**), a small amount of unreacted **1a** (2%), and three or four other unidentified products (5%).

For **1b**: $^{31}P\{^1H\}$ NMR shows peaks due to a major product (90%), assigned as [Ru(η^5-indenyl)(OH)(HP^iPr_2)(PPh_3)] (**8b-H**), a small amount of unreacted **1b** (2%), and two other unidentified products (8%).

(G) Addition of Methanol Monitored at Low Temperatures. For both samples, the thawed solution turned red, before being placed in the NMR spectrometer, which was precooled to 240 K. Complete conversion to a mixture of [Ru(η^5-indenyl)(OMe)(HPR_2)(PPh_3)] (**8-Me**) and [Ru(η^5-indenyl)(H)(HPR_2)(PPh_3)] (**9**) was immediate, with no residual **1** observed by $^{31}P\{^1H\}$ NMR. As the temperature was increased in 10 K increments to RT, signals for **9** increased in intensity at the expense of those for **8-Me**, until only **9** remained, along with ∼2% unidentified minor products. Both solutions were yellow when the warmed samples were removed from the spectrometer.

(H) Addition of *tert*-Butanol Monitored at Room Temperature. For **1a**: The mixed reagents retained the blue color of **1a**. $^{31}P\{^1H\}$ NMR shows mainly unreacted **1a** (77%), with peaks due to a minor product (15%) assigned as [Ru(η^5-indenyl)(OBu^t)($HPCy_2$)(PPh_3)] (**8a-Bu^t**), and five or six other unidentified products (8%).

For **1b**: The mixed reagents gave a red solution. $^{31}P\{^1H\}$ NMR shows mainly unreacted **1b** (50%), with peaks due to a minor product (36%) assigned as [Ru(η^5-indenyl)(OBu^t)($HPPr^t_2$)(PPh_3)] (**8b-Bu^t**), and three or four other unidentified products (14%).

(I) Additions of Diethyl Ether and THF to 1a,b Monitored at Room Temperature. The mixed reagents retained the blue color of **1a**,**b**. $^{31}P\{^1H\}$ NMR confirmed the continued presence of **1**, with only minor shift deviations (<0.5 ppm) arising from the added solvent.

(J) Addition of Acetone to 1a,b Monitored at Low Temperatures. In both cases, there was no immediate change in color as the mixture was thawed and placed in the precooled NMR spectrometer. $^{31}P\{1H\}$ NMR showed that, at 240 K, the samples were mainly unreacted **1a**,**b** (82−86%), along with peaks assigned to [Ru(η^5-indenyl)(CH_2COCH_3)(HPR_2)(PPh_3)] (**10a**,**b**, 14−15%), and one or two other unidentified products (1−3%). As the temperature was increased to 280 K in 10 K intervals, the intensity of peaks due to **10a**,**b** increased to 70−77%, at the expense of those due to **1a**,**b**. Upon further warming, the sample rapidly decomposed, giving (by $^{31}P\{^1H\}$ NMR) nine or 10 unidentified products at room temperature. After 1−2 days the sample was dark red and had further decomposed to a number of unidentified products, including some major species with peaks in the μ-phosphido region (240−100 ppm), with no residual **1a**,**b** or **10a**,**b**.

For **1a** at 260 K: $^{31}P\{^1H\}$ NMR shows unreacted **1a** (∼52%), **10a** (∼43%), and one or two unidentified products (∼5%).

For **1b** at 250 K: $^{31}P\{^1H\}$ NMR shows **10b** (∼60%), unreacted **1b** (∼42%), and an unidentified product (∼10%).

NMR-Scale Reactions of 3a and d$_3$-3a with KOBu^t. Solid **3a** (15 mg, 0.018 mmol), KOBu^t (5 mg, 0.045 mmol, 2.5 equiv), and O═PPh_3 (7.2 mg, 0.026 mmol, internal standard) were placed in a sealable NMR tube. d_8-Toluene (0.8 mL) was transferred under vacuum, and the tube was flame-sealed. The thawed solution was shaken to mix the reagents before being placed in the NMR spectrometer, where the progress of reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 15 min intervals for 1 h.

NMR-Scale Experiments Using 5a. These sealed samples were prepared using the same general method described above for **1a**,**b**.

(A) Addition of Acetonitrile. Solid **5a** (15 mg, 0.021 mmol) was used. At room temperature, over a 25 h period, the mixed reagents maintained the dark red color of **5a** and no change was observed in the $^{31}P\{^1H\}$ NMR spectrum. Even heating of the

(33) For these reactions, amounts of unreacted **1a**,**b** include 12% or 16% that exist as the phosphaalkene structural isomers (see ref 13).

(34) Peaks due to a species tentatively assigned as [Ru(η^5-indenyl)(NH_2CH_2Ph)(HPR_2)(PPh_3)] probably resulted from 1,2-addition to **1a**,**b** of α-aminotoluene, a known impurity in benzonitrile (Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Toronto, 1988; p 94). Consistent with this explanation is the observed decrease in relative intensity of these peaks (to ∼3%) when the reactions were repeated (at room temperature) with doubly distilled benzonitrile. However the ^{13}C-DEPT 135 NMR spectra of the reaction mixtures showed no benzylic carbons, and no α-aminotoluene was observed in the ^1H NMR spectra of purified benzonitrile: **1a**,**b** is apparently scavenging the trace amounts of α-aminotoluene present in the excess benzonitrile added.

sample at 65 °C for 4.5 h gave no spectroscopic changes, consistent with the irreversible coordination of CO in this complex.

(B) Addition of 1:1 Acetonitrile/d_3-Acetonitrile. Portions of solid **5a** (12 mg, 0.017 mmol) were used to prepare two sealed samples: one in d_8-toluene and one in d_0-toluene for analysis by ^{2}H NMR. The ^{1}H and ^{2}H NMR spectra were monitored over a 4 day period for signs of proton/deuteron exchange within the acetonitrile. Only a trace amount of CHD_2CN was observed (a triplet and a doublet in the ^{1}H and ^{2}H{^{1}H} NMR spectra, respectively), consistent with the standard 0.2% residual proton impurity in the commercial d_3-acetonitrile used.

Crystallographic Study of 2a. Orange crystals of **2a** were grown from diffusion of *n*-pentane into a toluene solution of the compound. Data were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer[35] using Mo Kα radiation ($\lambda = 0.71073$ Å) at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 6093 reflections from the data collection with $4.78° < 2\theta < 51.80°$. The space group was determined to be $P2_12_12_1$ (No. 19). The data were corrected for absorption through use of the SADABS procedure. The structure of **2a** was solved using the Patterson serach and structure expansion facilities within the DIRDIF-99 program system.[36] Refinement was completed using the program SHELXL-97.[37] The hydrogen atom attached to P1 was located and freely refined, while hydrogen atoms attached to carbons were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached atoms and were given thermal parameters 20% greater than those of the parent atoms. See Table 2 for a summary of crystallographic experimental parameters.

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Supporting Information Available: ^{1}H and ^{13}C NMR data for **2a**,**b** and **3a**,**b**; spectra illustrating sample purity, structure diagnosis and isotope labeling; details of line shape analyses and van't Hoff calculations, and a crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

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