Determination of Ruthenium−Phosphorus Bond Dissociation Energies by ES-FTICR Mass Spectrometry

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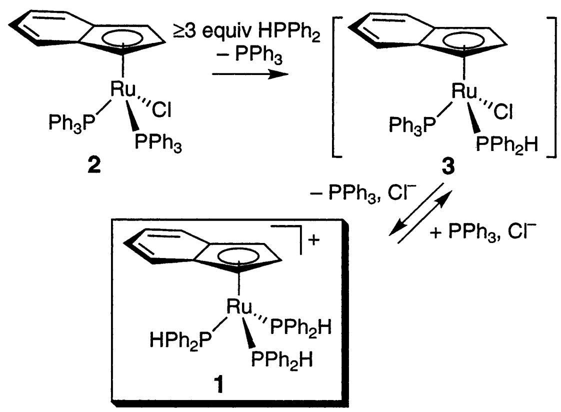
*Summary: Gas-phase activation energies have been estimated for the dissociation of one and two phosphines from the cationic ruthenium complex [(η^5-indenyl)Ru($HPPh_2)_3]^+$ (**1**) by the combined techniques of ES introduction and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry (MS). These values are 16.6 ± 2.3 and 34.6 ± 2.3 kcal mol^{-1}, respectively.*

Phosphine dissociation is critical to many organometallic reaction sequences. Metal−phosphine bond strengths are useful in the evaluation of possible mechanisms, particularly in catalysis, where important elementary steps can occur too quickly for in situ measurement of their thermal parameters. Despite the development of a range of techniques for probing metal−ligand bond energy information, both in solution and in the gas phase, the amassed library of organometallic bond energies remains extremely limited.[1] Among thermodynamic data collected, bond energies for metal complexes containing primary (1°) and secondary (2°) phosphines are particularly rare.

Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) provides extremely high mass resolution[2] and is a valuable tool for both qualitative and quantitative analysis of bond activation/reactions of ions in the gas phase.[3] This technique has been applied exhaustively to the study of ions generated from volatile precursors in the ICR cell (i.e. at very low pressures). Currently, the coupling of high-pressure introduction techniques such as electrospray (ES) with FTICR is of intense interest in analytical mass spectrometry.[4] The application of such coupled MS techniques to analysis of nonvolatile, solution-stable species is gradually expanding from the study of biological and organic molecules into the realm of inorganic chemistry.[5] Here we report the combined use of ES and FTICR-MS techniques to examine the fragmentation patterns of the cationic ruthenium(II) complex [(η^5-indenyl)Ru($HPPh_2)_3]^+$ (**1**) and to estimate energies for the dissociation of ruthenium−phosphorus bonds.

Scheme 1



We prepared complex **1** during our ongoing investigation of the reactions of (η^5-indenyl)Ru($PPh_3)_2$Cl (**2**) with 1° and 2° phosphines, in the context of catalytic P−H activation. Preliminary studies indicate some activity of **2** toward the hydrophosphination of acrylonitrile by 2° phosphines. The complex **1·Cl**$^-$ results from the addition of 3 equiv or more of diphenylphosphine to complex **2** (Scheme 1).[6] Monitoring of this reaction by $^{31}P\{^1H\}$ NMR spectroscopy indicates that a neutral complex, (η^5-indenyl)Ru(PPh_3)($HPPh_2$)Cl (**3**),[7] resulting from substitution of one of the two triphenylphosphine ligands in **2**, begins to form immediately upon addition of diphenylphosphine to **2**. Intermediate **3** remains in high concentration during the (much slower) formation of **1**.[8] Preliminary reactivity studies indicate that **1** will slowly convert to **3** in the presence of triphenylphosphine.[9]

The positive charge on complex **1**, along with its stability, made it straightforward to study by electrospray mass spectrometry (ES-MS).[10] Following well-established procedures for using ES-MS to determine relative labilities of ligands in metal complexes,[11] we varied the ES cone voltage[12] to either obtain the parent

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(5) See for example: (a) Henderson, W.; Nicholson, B. K.; McCaffrey, L. J. *Polyhedron* **1998**, *17*, 4291. (b) Hasselgren, C.; Fisher, K.; Jagner, S.; Dance, I. *Chem. Eur. J.* **2000**, *6*, 3671. (c) Satterfield, M.; Brodbelt, J. S. *Inorg. Chem.* **2001**, *40*, 5393. (d) Sautter, A.; Schmid, D. G.; Jung, G.; Würthner, F. *J. Am. Chem. Soc.* **2001**, *123*, 5424.

(6) See the Supporting Information for details of characterization and properties of **1**.

(7) $^{31}P\{^1H\}$ NMR for **3** (121.5 MHz, $CDCl_3$, δ): 50.9 (d, $^2J_{PP}$ = 45 Hz, $HPPh_2$). 47.5 (d, PPh_3).

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metal complex ion or promote ligand dissociation. At the minimum cone voltage, 80 V, the only ion type present is the intact cation **1** (major isotopic peak *m*/*z* 775). As the cone voltage is increased incrementally to 300 V, peaks appear due to first $[(C_9H_7)Ru(HPPh_2)_2]^+$ (**4**, *m*/*z* 589) and then $[(C_9H_7)Ru(HPPh_2)]^+$ (**5**, *m*/*z* 403), which correspond to dissociation of one and two $HPPh_2$ ligands, respectively, from **1**. At cone voltages above 140 V, there is also a small peak corresponding to the chloride-bound dimer[13] $[\{(C_9H_7)Ru(HPPh_2)_3\}_2(Cl)]^+$ (**6**). The remaining phosphine in **5** is resistant to Ru−P bond cleavage, but at higher cone voltages an ion formed by loss of C_6H_6 from **5** appears (major peak *m*/*z* 325). The (η^5-indenyl)-Ru core is apparently extremely robust: in these experiments, no ions were detected that could be attributed to indenyl-free ruthenium.

Having established possible fragmentation products for **1**, we further examined its behavior in the gas phase by placing the intact ion (produced from ES at a cone voltage of 80 V) in an FTICR cell. We performed collision-induced dissociation (CID) experiments,[14] in which a radio frequency pulse is applied to the ICR cell plates to increase the translational energies of mass-selected ions (e.g. intact **1**). These ions are then allowed to collide with a target gas for a defined period of time (CID delay), during which fragmentation may occur if the collisions are sufficiently energetic; resulting fragment ions can then be identified. The yields of fragment ions can be increased by increasing the translational energies of the intact ions or by increasing the number of collisions. Alternatively, if we can arrange for no more than a single collision between a reactant ion and the target gas during the CID delay, it should be possible to measure the threshold energy for fragmentation by studying collisions at steadily increasing collision energies.[15] We used this latter technique to estimate Ru−P bond dissociation energies involved in the fragmentation of **1** to give the ions $[(\eta^5\text{-indenyl})Ru(HPPh_2)_2]^+$ (**4**) and $[(\eta^5\text{-indenyl})Ru(HPPh_2)]^+$ (**5**).

Threshold energies for dissociation of one and two phosphines from **1** were determined by varying its collision impact with the target gas N_2. The relevant energy for collision, in an ICR cell, of a reactant ion such as **1** with a stationary target such as N_2 is the center-of-mass energy, E_{com}. This is a function both of the translational energy of the reactant ion and of the mass of the target relative to the total mass of reactant ion and target.[16] For the cell and conditions used in our experiments the collision energy is given by eq 1, in

$$E_{com} = (1.20607 \times 10^7)[m_{target}/(m_{ion} + m_{target})][(zV_{pp}t_{rf}S/d)^2/m_{ion}] \text{ eV/collision} \quad (1)$$

which the only two variable parameters are V_{pp} (the peak-to-peak voltage of the radio frequency pulse used to accelerate the parent ion) and t_{rf} (the duration of this radio frequency pulse).[17] In our experiments, ions entering the ICR cell[18] were translationally energized by a constant V_{pp} of 80 V, of controlled t_{rf}, and were subsequently allowed to collide with N_2 at a pressure of 1×10^{-8} mbar (as recorded by the manifold ion gauge). Since V_{pp} was held constant, the collision impact was directly controlled through variation of t_{rf}.

The frequency of collisions was estimated from eq 2, which is based on a previously derived equation[15] for the average time between collisions, $t_{collision}$, and adapted for our experimental conditions.[19] For $t_{rf} = 50$ μs (the

$$1/t_{collision} = (r_{ion} + r_{target})^2 PzV_{pp}t_{rf}S/[(8.983 \times 10^{-37})Tm_{ion}d] \quad (2)$$

approximate midpoint of the range of excitation times at which dissociation was detected by the mass spectrometer), under the conditions used in our experiments, the collision frequency is 2.60 collisions/s.[20] Our experiments[21] indicated that a CID delay of 0.05 s should give sufficient numbers of single collisions (~0.13 per ion) for measurable product ion yields,[22] while minimizing the number of double or multiple collisions.[23] We therefore used CID data from experiments with this delay time to estimate the threshold energies for phosphine dissociation from **1**.

Mass spectra of the ionic collision products showed that at sufficiently high collision energies loss of one or two phosphine ligands occurs, as in the ES experiments carried out at cone voltages greater than or equal to 100

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[8] This route to the tris-substituted **1** must also include substitution, in **3**, of either the remaining PPh_3 or the chloride, yielding (η^5-indenyl)$Ru(HPPh_2)_2Cl$ or $[(\eta^5\text{-indenyl})Ru(PPh_3)(HPPh_2)_2]^+Cl^-$, respectively, but so far neither of these bis(diphenylphosphine) intermediates has been observed by NMR spectroscopy.

[9] Friesen, D. M.; Rosenberg, L. Unpublished results.

[10] Techniques do exist for manipulating air- and moisture-sensitive compounds in ES experiments and also for activating neutral species for electrospray. (See ref 5a and references therein.)

[11] (a) Henderson, W.; Fawcett, J.; Kemmitt, R. D. W.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1995**, 3007. (b) Hori, H.; Ishitani, O.; Koike, K.; Takeuchi, K.; Ibusuki, T. *Anal. Sci.* **1996**, *12*, 587. (c) Hori, H.; Johnson, F. P. A.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Chem. Soc., Dalton Trans.* **1997**, 1019.

[12] Cone voltage refers to the potential difference between the electrospray nozzle and the skimmer, through which ions pass for mass detection. This value is also referred to as the nozzle-to-skimmer potential difference (PD).

[13] The dimeric structure is supported by the isotopic pattern observed.

[14] (a) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96. (c) Ions generated by electrospray are de-energized in a hexapole ion trap prior to injection into the ICR cell.

[15] Hop, C. E. C. A.; McMahon, T. B.; Willett, G. D. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 191.

[16] Shukla, A. K.; Futrell, J. H. *Mass Spectrom. Rev.* **1993**, *12*, 211.

[17] In eq 1, m_{target} and m_{ion} are the masses (in atomic mass units) of the target molecule and reactant ion, respectively, *z* is the number of charges on the reactant ion, *S* (=0.814) is the geometry factor for the 6 cm × 6 cm cylindrical ICR cell, and *d* is the diameter of the cell (0.060 m).

[18] A correlated sweep centered on *m*/*z* 775 was used to ensure that only intact **1** entered the ICR cell. See the Supporting Information for details.

[19] In eq 2, r_{ion} and r_{target} are the average radii (in m) of the ion and target molecule, *P* (in atm) is the pressure of the target gas, *T* (K) is the temperature of the cell/target gas, and the other symbols are as defined above.

[20] For the calculation of collision frequency, $m_{ion} = 775$, $r_{ion} + r_{target} = 1 \times 10^{-9}$ m, $P = 10^{-11}$ atm, $z = 1$, $V_{pp} = 80$ V, $S = 0.814$, $T = 300$ K, and $d = 0.06$ m. Uncertainty in the result arises from estimates (see Supporting Information) of the effective collision radii and the efficiency of energy transfer in the collisions, since some of the collisions will be glancing (a minority, based on the relative sizes of the projectile ion and the target molecule). However, the largest uncertainties stem from the potential error in the measured N_2 pressure in the collision cell (vide infra).

[21] See the Supporting Information for details of the choice of CID delay times.

[22] More detailed analysis (vide infra) indicates that this estimate is too low but confirms that single-collision conditions do predominate for a CID delay of 0.05 s.

[23] Kim, M. S. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 189.

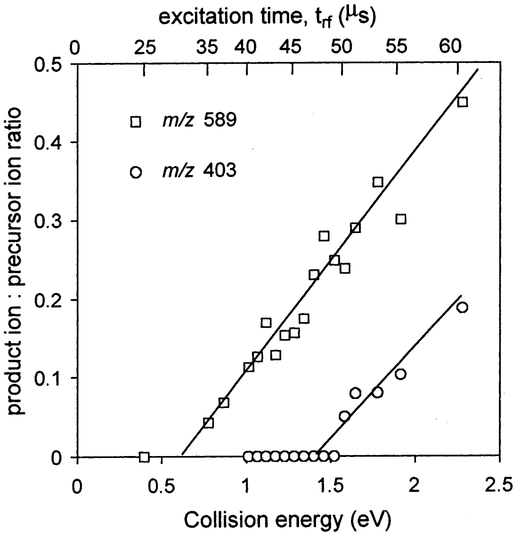

Figure 1. Normalized product ion to precursor ion ratios from CID experiments on **1** (*m/z* 775).

V. The normalized abundance[24] of each of the product ions **4** and **5**, relative to that of the parent ion **1**, was plotted as a function of the calculated collision energies, as shown in Figure 1.[25] The plots in Figure 1 appear to have extended linear regions, as is typical above threshold in collision experiments,[26] despite the probable increasing importance of multiple collisions as t_{rf} increases. Although the random thermal motion of the target molecules and the parent ions prior to acceleration can introduce a spread in the center-of-mass collision energy, in these experiments the thermal motion of the parent ion (**1**) prior to acceleration is negligible in this context.[27] However, the thermal motion of the target molecule (N_2) does influence the computed threshold curves shown in Figure 1, producing curvature prior to the beginning of the linear portion. Thus, extrapolation of the linear portion back to a zero abundance of product ions does not provide a true value of E_{com}(threshold) but instead gives E_{com}(threshold) − $3\gamma kT$, where $\gamma = m_i/(m_i + m_t)$, k is the Boltzmann constant, and T is the temperature of the target gas. In our experiments this correction term is small: at 300 K, with $m_i = 775$ and $m_t = 28$, we find $3\gamma kT = 0.075$ eV/molecule (=1.8 kcal/mol = 7.2 kJ/mol). The plots for dissociation of one and two phosphine ligands from **1** extrapolate to axis values of 0.642 ± 0.095 and 1.428 ± 0.087 eV, respectively.[28] Adding the 0.075 eV correction term to these values gives E_{com}(threshold) values of 0.72 ± 0.10 eV and 1.50 ± 0.10 eV for the dissociation processes, respectively. Thus, our estimated dissociation energy for loss of one phosphine ligand from **1** is 69.5 ± 10 kJ mol^{-1} (16.6 ± 2.3 kcal mol^{-1}) and for dissociation of two ligands is 145 ± 10 kJ mol^{-1} (34.6 ± 2.3 kcal mol^{-1}).

In the context of the potential participation of complexes **1**−**3** in catalysis, the dissociation energy calculated for loss of just one phosphine from **1**, to give the 16-electron cation **4**, is most relevant. Substitution of this first phosphine is critical for further reactivity at the (indenyl)Ru core in **1**, to pull this complex (back) into a catalytic cycle, and previous studies of **2** have shown phosphine substitution reactions at this (indenyl)Ru fragment to proceed by dissociative mechanisms.[29] Our estimated Ru−PPh_2H dissociation energy of 16.6 kcal mol^{-1} falls between values for a Ru−PPh_3 bond (BDE = 14.0 kcal mol^{-1}) and a Ru−PPh_2Me bond (BDE = 19.7 kcal mol^{-1}) calculated from solution calorimetry studies of a series of substitution reactions of phosphines at the neutral Cp*RuCl core.[30] The strong dependence of phosphine basicity (as gauged by pK_b values)[31] on the inductive effects of substituents at phosphorus[32] suggests that diphenylphosphine should bind less strongly than either PPh_2Me or PPh_3. However, for 3° phosphines, at least, Ru−P bond enthalpies at Cp*RuCl correlate much more strongly with the relative bulkiness of the phosphine than with electronic features. In this context our calculated value might be expected to be somewhat higher than the 19.7 kcal mol^{-1} reported for Ru−PPh_2Me. Our estimated value may represent a balance point for electronic and steric parameters that is unique to 2° phosphines (by comparison with 3° phosphines). This can only be verified by collecting similar data for analogous cationic complexes of a broad range of secondary phosphines.

The Cp*Ru−P bond energies determined from the measured enthalpies of a series of substitution reactions apply only within that system under the conditions used (e.g. solvent, temperature). In contrast, our estimated, gas-phase dissociation energies are absolute. There are concerns over inaccuracies in CID-derived bond dissociation energy data, which may arise from the variety of (unknown) vibrational and rotational excited states involved before and after an ion/molecule collision.[33] In this context and given the inherent lack of dynamic range and sensitivity of the ICR technique relative to, for example, ion beam methods,[34] our estimated Ru−P BDE values must be considered *minimum* values. Nonetheless, the ES-FTICR-CID technique has the potential for rapid determination of useful bond dissociation energies in organometallic complexes. Ideally, calorimetry and ES-MS techniques such as FTICR-CID could provide complementary data, allowing correlation

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(24) To account for the increase in collision frequency with t_{rf}, the ion ratios plotted in Figure 1 were normalized to the ratio at t_{rf} = 50 μs by multiplying the ratio at t_{rf} = 50 μs by 50/*x*, where *x* is the excitation time for the measurement.

(25) These data imply a collision probability of 0.80, rather than the 0.13 estimated from eq 2. This may be attributed to a N_2 pressure in the ICR cell ≈6 times higher than that recorded by the manifold ion gauge. See ref 22 and the Supporting Information for details of the calculation of collisional probabilities for these Poisson distributions.

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(27) Chantry, P. J. *J. Chem. Phys.* **1971**, *55*, 2746.

(28) See the Supporting Information for details of the linear regression analysis.

(29) Gamasa, M. P.; Gimeno, J.; Gonzalez-Bernardo, C.; Martin-Vaca, B. M.; Monti, D.; Bassetti, M. *Organometallics* **1996**, *15*, 302.

(30) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781. These experiments gave Ru−PR_3 dissociation energies ranging from 9.4 to 23.8 kcal mol^{-1}.

(31) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley: New York, 2000.

(32) Estimated electronic parameters for phosphines indicate a decrease in ligand donor ability with variation of substituents in the order Me > Ph > H: Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(33) The similarity of our BDE values to those measured by solution calorimetry for Cp*Ru systems is reassuring on this count. Inaccuracies arising from a range of accessible vibrational/rotational states may be insignificant on the scale of BDE being measured and within the levels of precision possible for the FTICR technique.

(34) Armentrout, P. B. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 419.

of metal–ligand bond strength trends, established by solution calorimetry, with absolute (if minimum) bond strengths provided by mass spectrometric studies of intact, solution-stable organometallic complexes.

We have recently prepared cationic analogues of **1**, which contain other secondary phosphines or mixtures of two primary phosphines and a single triphenylphosphine. Our continued study of this system of complexes using combined ES-FTICR-MS will allow us to create a useful library of minimum Ru–P bond dissociation energies and to probe, in the mixed-phosphine complexes, the relative binding affinities of 1° and 3° phosphines.

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Supporting Information Available: Text giving full synthetic and mass spectrometric experimental details and figures giving descriptions of the equipment used in these experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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