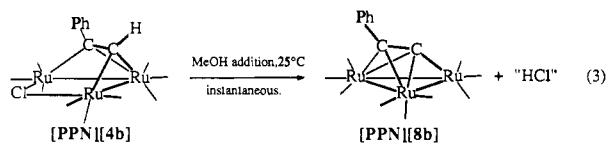


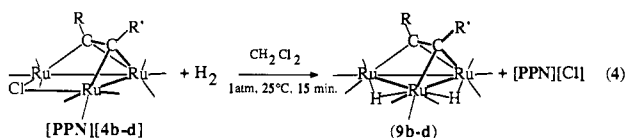
crystallized, 60%).¹² The X-ray structure of **6d** has been determined.¹²

The known bis-alkyne derivative $\text{Ru}_3(\mu\text{-}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5))_2(\text{CO})_8$ (**7c**) is readily obtained from [PPN][**4c**] upon addition of [Ag][BF₄] in the presence of alkyne.^{14,15} The structure of this complex has now been determined.¹⁶

In attempts to prepare the elusive species " $\text{Ru}_3(\mu\text{-RCCR}')(\text{CO})_9$ ",^{6a,17} we have carried out the reaction of [PPN][$\text{Ru}_3(\mu\text{-Cl})(\mu\text{-RCCR}')(\text{CO})_9$] with protic solvents in the absence of ligand. In the case of phenylacetylene (reaction 3), immediate precipitation of the known¹⁸ acetylide species [PPN][$\text{Ru}_3(\mu_3\text{-CC}(\text{C}_6\text{H}_5))(\text{CO})_9$] ([PPN][**8b**]) is observed.¹⁹



A rapid displacement of the halide by hydrogen from [PPN][**4b-d**] takes place under ambient conditions in dichloromethane solution (reaction 4) to give selectively the known²⁰ neutral dihydrido species $\text{Ru}_3(\mu\text{-H})_2(\mu\text{-RCCR}')(\text{CO})_9$ (**9b-d**) within 15-20 min.²¹



The neutral complex **9** is not seen when reaction 4 is carried out in THF; instead, the complexes [PPN][$\text{Ru}_3(\mu\text{-H})(\mu\text{-RCCR}')(\text{CO})_9$] ([PPN][**10**]), [PPN][$\text{HRu}_3(\text{CO})_{11}$], and [PPN][$\text{H}_3\text{Ru}_4(\text{CO})_{12}$] are identified in solution. As noted earlier,^{3a} under highly dissociating conditions, the halide becomes sufficiently nucleophilic to deprotonate a hydrido cluster complex. The new species [PPN][**10**] is obtained selectively by the following procedures: (i) deprotonation of **9** by [PPN][Cl] (80-90% yield), (ii) hydrogenation of [PPN][**4**] in ethanol (25 °C, 15 min, 70-80% yield), (iii) treatment of [PPN][**4**] with [PPN][BH₄] in THF (100% spectroscopic yield), and (iv) direct reaction of an alkyne with [$\text{HRu}_3(\text{CO})_{11}$]⁻ (THF, 25 °C, 4 h, 40-50% yield).²¹ An X-ray structure analysis of [PPN][$\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5))(\text{CO})_9$] ([PPN][**10c**])²² reveals that the alkyne is coord-

inated in a $\mu_3\eta^2\text{-}\parallel$ mode on the face of a closed metal triangle where the bridging hydride ligand occupies the same edge as the halide in the antecedent species [PPN][**4c**].

There is now evidence to suggest that the synthetic applications of halide-promoted ruthenium cluster anions are matching those of the classic procedure using trimethylamine *N*-oxide/CH₃CN,⁷ with the additional advantage that enhanced activity toward hydrogen is also observed, parallel to the behavior of related activated cluster complexes.^{23,24}

Acknowledgment. This work was supported by the C.N.R.S. We are grateful to Johnson-Matthey for generous loans of ruthenium trichloride.

Supplementary Material Available: Experimental details for the preparation and characterization of the complexes (supplement to footnotes 5, 12, 19, and 21) and crystallographic data for the complex [PPN][**4c**], including listings of atomic coordinates, anisotropic thermal parameters, and selected interatomic distances and bond angles (13 pages); a listing of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

(23) Taube, D. J.; Rokicki, A.; Anstock, M.; Ford, P. C. *Inorg. Chem.* **1987**, *26*, 526-530.

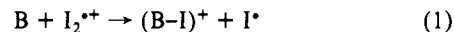
(24) In our hands, [PPN][$\text{Ru}_3(\mu\text{-H})(\text{CO})_{11}$] is quantitatively obtained by reaction of [PPN][$\text{Ru}_3(\eta^1\text{-Cl})(\text{CO})_{11}$] ([PPN][**2**]) with H₂ at 25 °C (1 atm, 25 °C, THF, 10-15 min).

Structural Effects on the Iodine Cation Basicity of Organic Bases in the Gas Phase

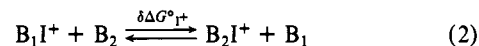
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Electron-impact ionization¹ of iodine vapor leads to the formation of I₂^{•+}(g). A Fourier transform ion cyclotron resonance spectrometry (FTICR)³ study of the reactivity of this ion⁴ has revealed the existence of new gas-phase ion-molecule reactions, the most important being as follows: (1) the displacement of I⁺ by *n*-donor bases (B), reaction 1,



this process generally being followed by the formation of clusters, (B)_{*n*}⁺;⁵ (2) the exchange of iodine cation between different bases (B₁, B₂), reaction 2,



Double resonance experiments indicate the reversibility of the iodine cation exchange. Figure 1 is the mass spectrum of a mixture

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(1) Ionization energies in the 15-25-eV range.

(2) Under our working conditions, the small amount of I⁺ initially formed undergoes an electron-transfer reaction with I₂ and does not contribute to the reactions described in this work.

(3) (a) Lehman, A. T.; Bursey, M. M. *Ion Cyclotron Resonance Spectrometry*; John Wiley: New York, 1976. (b) Laukien, F. H.; Allemann, M.; Bischofberger, P.; Grossmann, P.; Kellerhals, P. In *Fourier Transform Mass Spectrometry, Evolution, Innovation and Applications*; Buchanan, M. V., Ed.; ACS Symposium Series 359; American Chemical Society: Washington, DC, 1987; Chapter 5.

(4) Experiments have been performed on a modified Bruker CMS-47 FTICR mass spectrometer under a magnetic field strength of 4.7 T. Because of the very reliable relative ion intensities it provides, the rapid scan/cross correlation method^{3b,19} has been used throughout this work.

(5) Pyridine (Py) and molecular iodine react in dipolar, aprotic solvents to yield PyI⁺ and Py₂I⁺ (Poskin, G.; Huyskens, P. *Bull. Soc. Chim. Fr.* **1976**, 337 and references therein).

(14) $\text{Ru}_3(\mu\text{-}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5))_2(\text{CO})_8$ (**7c**):^{5a} IR (ν_{CO} (cm⁻¹), CH₂Cl₂) 2077s, 2047 vs, 2022 vs, 1990 m, 1962 m.

(15) (a) Ros, R.; Scriveranti, A.; Albano, V. G.; Braga, D.; Garlashedi, L. *J. Chem. Soc., Dalton Trans.* **1986**, 2411-2421. (b) Ros, R.; Scriveranti, A.; Roulet, R. *J. Organomet. Chem.* **1986**, *303*, 273-282. (c) Nicholls, J. N.; Raithby, P. R.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1617-1619.

(16) (a) Crystal data for **7c**: monoclinic, C2/c, No. 15, *a* = 38.440 (7) Å, *b* = 8.544 (2) Å, *c* = 22.002 (2) Å, β = 114.67 (1)°, *V* = 6566 (30) Å³, *Z* = 8; *R* = 0.025 and *R*_w = 0.032 (from 4843 observations). Details will be reported in the full paper. The overall geometry is related to that of the osmium analogue.^{16b,c} (b) Johnson, B. F. G.; Khattar, R.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1987**, *319*, C51-C57. (c) Housecroft, C. E.; Owen, S. M. *J. Organomet. Chem.* **1988**, *339*, 139-149.

(17) (a) There is still some doubt about the existence of this species.^{17b} (b) Busetti, V.; Granozzi, G.; Aime, S.; Gobetto, R.; Osella, D. *Organometallics* **1984**, *3*, 1510-1515.

(18) Barner-Thorsen, C.; Hardcastle, K. I.; Rosenberg, E.; Siegel, J.; Manotti Lanfredi, A. M.; Tiripicchio, A.; Tiripicchio Camellini, M. *Inorg. Chem.* **1981**, *20*, 4306-4311.

(19) [PPN][**8b**]:^{5a} IR (ν_{CO} (cm⁻¹), THF) 2046 m, 2003 vs, 1994 vs, 1966 s, 1945 m.

(20) (a) Gambino, O.; Sappa, E.; Cetini, G. *J. Organomet. Chem.* **1972**, *44*, 185-188. (b) Churchill, M. R.; Fettinger, J. C.; Keister, J. B.; See, R. F.; Ziller, J. W. *Organometallics* **1985**, *4*, 2112-2116.

(21) (a) **9b**:^{5a} IR (ν_{CO} (cm⁻¹), cyclohexane) 2103 w, 2078 m, 2050 vs, 2040 w, 2012 s, 1997 ms, 1981 w, 1970 vw; ¹H NMR (CDCl₃) δ 9.2 (s, CH), 15.0 (s, hydride), 18.7 (s, hydride). (b) [PPN][**10c**] (85% yield):^{5a} IR (ν_{CO} (cm⁻¹), THF) 2052 m, 2024 s, 1990 vs, br, 1975 m, 1955 mw; ¹H NMR (CDCl₃) δ -19.0 (s, 1 H, hydride).

(22) Crystal data for [PPN][**10c**]: fw = 1273.14, triclinic $\bar{P}1$, No. 2, *a* = 15.654 (2) Å, *b* = 17.447 (3) Å, *c* = 10.667 (1) Å, α = 99.87 (1)°, β = 99.12 (1)°, γ = 101.51 (1)°, *V* = 2755 Å³, *Z* = 2, μ (Mo K α) = 8.24 cm⁻¹; *R*_w = 0.049 and *R* = 0.047 for 6445 unique reflections. Full details will be provided in the full paper.

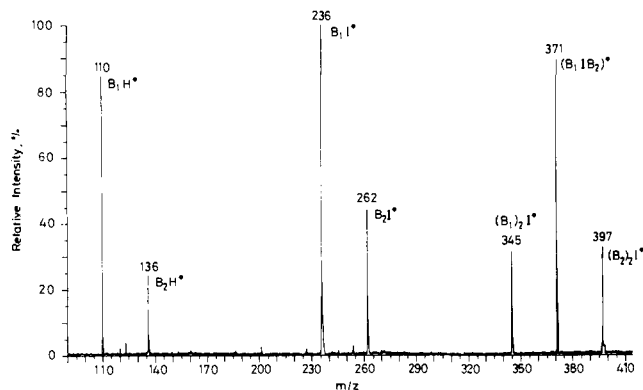
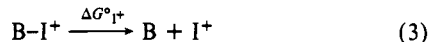


Figure 1. Mass spectrum of a 1:2.3:4 mixture of 4-methoxypyridine (B_1), 4-*tert*-butylpyridine (B_2), and I_2 . Nominal pressure: 3.0×10^{-6} mbar. Reaction time: 7 s.

of iodine, 4-*tert*-butylpyridine, and 4-methoxypyridine, illustrating reaction 1.

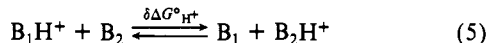
Reaction 2 allows the construction of a scale of iodine cation basicity (ICB), defined as the standard free energy change, $\Delta G^\circ_{I^+}$, for reaction 3 in the gas phase:



The ICB can be compared to proton gas-phase basicity, GB, defined as the standard free energy change, $\Delta G^\circ_{H^+}$, for reaction 4 in the gas phase:



In favorable cases (such as the one shown in Figure 1), both proton exchange and iodine cation exchange can be observed simultaneously. This allows the simultaneous determination of $\delta\Delta G^\circ_{I^+}$ and $\delta\Delta G^\circ_{H^+}$, the standard free energy changes for reactions 2 and 5 in the gas phase:⁶



Structural effects on the ICBs of selected organic molecules are summarized in Chart I together with the GBs (relative to NH_3) for the same compounds. All values are given at 333 K.⁷ $\delta\Delta G^\circ_{I^+}$ and $\delta\Delta G^\circ_{H^+}$ values for pyridine (Py) and a set of nine substituted pyridines are related through eq 6, Py being chosen as the reference base, B_1 :

$$\delta\Delta G^\circ_{I^+} = (0.07 \pm 0.05) + (0.444 \pm 0.012)\delta\Delta G^\circ_{H^+} \quad (6)$$

in kcal mol^{-1} ($n = 10$; $r^2 = 0.998$; $SD = 0.07 \text{ kcal mol}^{-1}$). Equation 6 shows that substituent effects on GB and ICB are proportional, provided the reaction center is kept constant and steric hindrance is minimal.

Reaction 1 is not observed with π -bases (hexamethylbenzene) or oxygen bases such as aliphatic alcohols, ethers, ketones, and esters,¹¹ but N,N-substituted amides and tertiary amines undergo both reactions 1 and 2. Of special interest is the high ICB of tetrahydrothiophene, the weakest proton acceptor shown in Chart I. Comparison of these findings with data obtained in the gas

Chart I. Ranking of Gas-Phase ICBs for X-Substituted Pyridines and Other Organic Compounds^a

$\Delta G^\circ_{I^+}$ (kcal.mol ⁻¹)	Base	$\Delta G^\circ_{H^+}$ (kcal.mol ⁻¹)
	(CH ₂) ₄ S	(-0.6) ^(a)
	c-C ₆ H ₁₁ N(CH ₃) ₂	(-29.4) ^(a)
	(C ₂ H ₅) ₃ N	(-29.4) ^(a)
	X = 4-OCH ₃	(-24.8) ^(a)
	X = 4- <i>t</i> -C ₄ H ₉	(-23.4) ^(b)
	X = 4- <i>i</i> -C ₃ H ₇	(-22.8) ^(c)
	X = 4-C ₂ H ₅	(-21.9) ^(b)
	X = 4-CH ₃	(-21.2) ^(a)
	X = 3-CH ₃	(-20.4) ^(a)
	X = H	(-17.7) ^(a)
	X = 4-CO ₂ CH ₃	(-15.4) ^(b)
	X = 4-COCH ₃	(-14.3) ^(c)
	X = 4-Cl	(-14.3) ^(a)
	DMF	(-8.1) ^(a)

^a Values in parentheses are GBs relative to NH_3 , defined as in eq 5 with $B_1 = NH_3$. (The larger the GB, the more negative the value of $\Delta G^\circ_{H^+}$.) (a) Reference 8. (b) Reference 9. (c) Reference 10.

phase¹² and in solution¹³ indicates that I^+ behaves as a soft acid.¹⁴ The B-I bonds examined in this work have a heterolytic bond strength of at least $65.5 \text{ kcal mol}^{-1}$ ¹⁵ in order for reaction 1 to be exothermic. These bonds are also likely to have substantial covalent character, as indicated by the relatively small ICB of amides relative to amines. The slope in eq 6 is 0.44. A value of 0.49 ± 0.02 is found for the slope of a plot of $\delta\Delta G^\circ_{Li^+}$ (differential gas-phase lithium cation basicity, LCB) vs $\delta\Delta G^\circ_{H^+}$ for a series of 3- and 4-substituted pyridines.^{16a} This is striking, for the low $\delta\Delta G^\circ_{Li^+}/\delta\Delta G^\circ_{H^+}$ ratios have been taken as indicative of the small covalent character of the B-Li bonds in BLi^+ .¹⁷ Steric effects are likely to be responsible for the different $\Delta G^\circ_{I^+}$ values for (C₂H₅)₃N and c-C₆H₁₁N(CH₃)₂.¹⁸

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(12) For example, with CH_3Hg^+ (Stone, J. A.; Splinter, D. E. *Can. J. Chem.* **1981**, *59*, 1779).

(13) (a) Marcus, Y. *J. Phys. Chem.* **1987**, *91*, 4422. (b) Persson, I. *Pure Appl. Chem.* **1986**, *58*, 1153.

(14) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423.

(15) As deduced from the adiabatic ionization potential of I_2 , 9.22 eV (Potts, A. W.; Price, W. C. *Trans. Faraday Soc.* **1971**, *1242*), the bond dissociation energy of I_2 , 36.456 kcal mol⁻¹ (Le Roy, R. J.; Bernstein, R. B. *Chem. Phys. Lett.* **1970**, *5*, 42), and the ionization potential of I, 10.44 eV (*Landolt-Börnstein Zahlenwerte und Funktionen*; Band I, Teil I, Berlin, 1950, p 212). The correction for the "electron at rest" reference state of this value amounts to 1.0 kcal mol⁻¹.

(16) (a) Anvia, F.; Walsh, S.; Taft, R. W.; de Paz, J. L. G.; Catalán, J., to be submitted. (b) Gal, J.-F.; Maria, P.-C. *Prog. Phys. Org. Chem.*, in press. (c) Alcamí, M.; Mío, O.; Yáñez, M. *J. Phys. Chem.*, in press.

(17) (a) See, e.g., ref 16b and references therein. (b) The ionic character of the B-Li⁺ bond gives DMF a LCB close to that of 4-(*N,N*-dimethylamino)pyridine, that for (CH₃)₃N being less than for CH₃CN.^{16a}

(18) The ions (C₂H₅)₃NI⁺ and c-C₆H₁₁(CH₃)₂NI⁺ undergo other reactions. They shall be described in due course.

(19) (a) McIver, R. T., Jr.; Hunter, R. L.; Ledford, E. B.; Locke, M. J.; Franch, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65. (b) Parisod, G.; Gaumann, T. *Chimia* **1980**, *34*, 271.

(6) Under these conditions, the ratio, ρ , of the relevant ion intensities, $\rho = ([B_1H^+]/[B_2H^+])/([B_2I^+]/[B_1I^+])$, can be directly obtained; then $\delta\Delta G^\circ_{I^+} - \delta\Delta G^\circ_{H^+} = RT \ln \rho$. ρ is independent of the pressures of the reagents, and $\delta\Delta G^\circ_{I^+} - \delta\Delta G^\circ_{H^+}$ can be determined very precisely.

(7) This is the temperature determined next to, and near the center of, a receiver plate of the ICR cell. Values of $\Delta G^\circ_{H^+}$ relative to NH_3 , not determined in this work, have been corrected to 333 K by using the corresponding proton affinities. This correction amounts to 0.1 kcal mol⁻¹ or less.

(8) Private communication from Prof. R. W. Taft and Dr. F. Anvia. See also: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(9) From the compilation given by the following: Abboud, J.-L. M.; Catalán, J.; Elguero, J.; Taft, R. W. *J. Org. Chem.* **1988**, *53*, 1137.

(10) Determined in this work. Experimental results as indicated in Chart I.

(11) Some of these compounds may undergo reaction 2, provided I^+ is made available from a source other than reaction 1. See, e.g.: Tikhonov, A. A.; Sokolov, V. V.; Keruze, Yu. I.; Grishin, N. N. *Zh. Org. Khim.* **1985**, *21*(12), 2482.