Halide-Promoted Reactions of Alkynes with $Ru_3(CO)_{12}$

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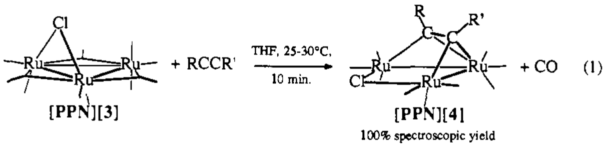
The promoter effect of anionic nucleophiles on reactions of metal carbonyl complexes is of high current interest.[1] In particular, several novel catalytic processes of potential industrial relevance are based on $Ru_3(CO)_{12}$/halide systems as catalyst precursors.[2] Besides, the association of anionic nucleophiles with $Ru_3(CO)_{12}$ in aprotic solvents gives a series of interconvertible cluster anions exhibiting enhanced activity.[1,3]

In attempts to extend earlier observations of a base-promoted catalytic CO displacement by phosphines from $Ru_3(CO)_{12}$ (**1**)[3a,4] to the case of unsaturated organic ligands, we have found that the activated complex $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ ([PPN][**3**]), which is readily obtained from the initial halide adduct $[PPN][Ru_3(\eta^1\text{-}Cl)(CO)_{11}]$ ([PPN][**2**][3a,h,i]) {PPN = bis(triphenylphosphine)iminium}, reacts with alkynes at 25 °C in THF (reaction 1) to produce a labile species $[PPN][Ru_3(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}RCCR')(CO)_9]$ ([PPN][**4**])[5] that serves as a convenient precursor to new and known[6,7] alkyne-substituted derivatives of $Ru_3(CO)_{12}$.



(1)

RCCR' = (**a**) acetylene, (**b**) phenylacetylene, (**c**) diphenylacetylene, (**d**) dimethylacetylene

The structure of [PPN][**4c**] is shown in Figure 1.[8]

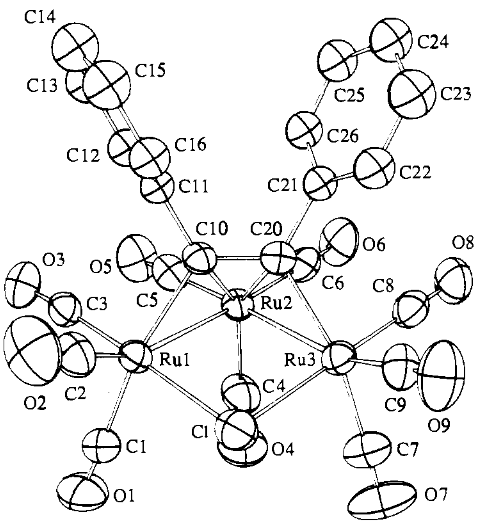
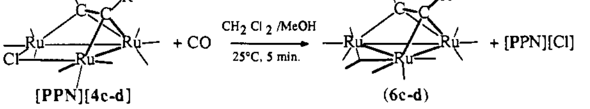


Figure 1. Perspective view of the anionic unit of the complex $[PPN][Ru_3(\mu\text{-}Cl)(\mu\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][**4c**]). Selected interatomic distances and bond angles: Ru(1)–Ru(2) = 2.777 (1) Å; Ru(2)–Ru(3) = 2.775 (1) Å; Ru(1)···Ru(3) = 3.659 (1) Å; Ru(1)–Ru(2)–Ru(3) = 82.46 (3)°; bridging halide located 0.579 (2) Å below the metal triangle; Ru(1)–Cl = 2.453 (2) Å; Ru(3)–Cl = 2.457 (2) Å; Ru(1)–Cl–Ru(3) = 96.36 (7)°; Ru(1)–C(10) = 2.117 (6) Å; Ru(2)–C(20) = 2.254 (7) Å; Ru(2)–C(10) = 2.240 (7) Å; Ru(3)–C(20) = 2.113 (6) Å.

The formation of [PPN][**4**] from [PPN][**3**] may involve a transition state where the edge-bridging halide becomes a triply bridging position to labilize an axial CO ligand on the unique ruthenium center, parallel to the behavior of iodide[9] and other ancillary bridging ligands.[10] Indeed, we also find that addition of alkynes to $[PPN][Ru_3(\mu_3\text{-}I)(CO)_9]$ ([PPN][**5**]) gives the iodide analogue of [PPN][**4**].

A characteristic feature of [PPN][**4b–d**][5] is that *halide displacement from the cluster is catalyzed by a protic solvent*, a reaction that is reminiscent of earlier observations in the chemistry of mononuclear halide complexes.[11] For example, though [PPN][**4d**] is unreactive toward CO at 25 °C in THF or dichloromethane, rapid substitution takes place upon addition of methanol (reaction 2) to yield $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (**6d**) selectively.[12,13]



(2)

Reaction 2 is reversed instantaneously in THF and at slower rates in other solvents. A clean extraction procedure avoiding chromatographic workup is carried out from a biphasic methanol/hexane mixture: the neutral complex **6** formed under CO in the methanol phase is recovered in the hexane phase (yield,

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[1] (a) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139–217. (b) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter 4, pp 43–88. (c) Lavigne, G. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; Verlag Chemie, in press. (d) Kaesz, H. D. In the Mond Centennial Volume of *J. Organomet. Chem.*, in press.

[2] (a) Dombek, B. D. *Organometallics* **1985**, *4*, 1707–1712 and references therein. (b) Knifton, J. *J. Mol. Catal.* **1988**, *47*, 99–116 and references therein. (c) Knifton, J. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1988; Vol. 6, pp 1–58 and references therein. (d) Yoshida, S.-I.; Mori, S.; Kinoshita, H.; Watanabe, Y. *J. Mol. Catal.* **1987**, *42*, 215–227. (e) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1988**, *53*, 1243–1250 and references therein. (f) Bhaduri, S.; Khwaja, H.; Sharma, K.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1989**, 515–516.

[3] (a) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647–4648. (b) Darensbourg, D. L.; Gray, R. L.; Pala, M. *Organometallics* **1984**, *3*, 1928–1930. (c) Anstock, M.; Taube, D.; Cross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696–3697. (d) Zuffa, J. L.; Blohm, M. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 552–553. (e) Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4669–4671. (f) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *J. Chem. Soc., Chem. Commun.* **1987**, 957–958. (g) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3426–3428. (h) Han, S.-H.; Geoffroy, G. L.; Dombek, B. D.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4355–4361. (i) Chin-Choy, T.; Harrison, W. T. A.; Stucky, G. D.; Keder, N.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 2028–2029.

[4] Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Inorg. Chem.* **1987**, *26*, 2345–2347.

[5] (a) Experimental details for the preparation and characterization of all complexes reported in this study are provided in the supplementary material. (b) [PPN][**4a**]:[5a] IR (ν_{CO} (cm^{-1}, THF) 2056 mw, 2031 vs, 1985 vs, br, 1949 m, 1918 w. (c) [PPN][**4c**]:[5a] yield 87%; IR (ν_{CO} (cm^{-1}), CH_2Cl_2) 2056 mw, 2035 vs, 1985 vs, br, 1955 m, 1915 w.

[6] For thermal reactions, see: (a) Cetini, G.; Gambino, O.; Sappa, E.; Valle, M. *J. Organomet. Chem.* **1969**, *17*, 437–443. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203–239 and references therein.

[7] Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *296*, 147–153.

[8] Crystal data for [PPN][**4c**]: triclinic $P\bar{1}$, No. 2, a = 15.913 (4) Å, b = 16.307 (4) Å, c = 10.992 (4) Å, α = 82.73 (2)°, β = 98.55 (3)°, γ = 103.21 (4)°, V = 2733 Å^3, Z = 2, μ(Mo Kα) = 9.65 cm^{-1}; data collection at 20 °C on an Enraf-Nonius CAD4; direct methods (SHELX86) and least-squares refinement; R_w = 0.046 and R = 0.045 for 6490 reflections.

[9] Kampe, C. E.; Boag, N. M.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390–1397.

[10] (a) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 392–399. (b) Dalton, D. M.; Barnett, D. J.; Duggan, D. J.; Keister, J. B.; Malik, P. T.; Modi, S. P.; Shaffer, M. R.; Smesko, S. A. *Organometallics* **1985**, *4*, 1854–1866.

[11] Schenk, W. A. *J. Organomet. Chem.* **1979**, *179*, 253–261.

[12] (a) **6d**:[5a] IR (ν_{CO} (cm^{-1}), cyclohexane) 2091 m, 2052 vs, 2049 sh, 2025 s, 2005 ms, 1972 vw, 1880 mw; ^{1}H NMR ($CDCl_3$) δ 2.3 (s, CH_3). (b) Crystal data for **6d**: monoclinic $P2_1/c$, No. 14, a = 14.716 (1) Å, b = 14.153 (2) Å, c = 18.226 (2) Å, β = 96.70 (2)°, V = 3770 Å^3, Z = 8 (two identical cluster molecules in the asymmetric unit); final R = 0.030 and R_w = 0.037. Details will be reported in the full paper.

[13] For the osmium analogue of **6**, see: Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636–639.

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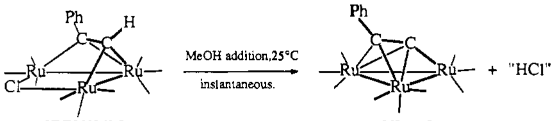
crystallized, 60%).[12] The X-ray structure of **6d** has been determined.[12]

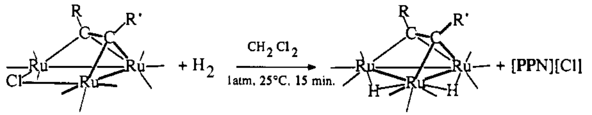
The known bis-alkyne derivative $Ru_3(\mu\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (**7c**) is readily obtained from [PPN][**4c**] upon addition of $[Ag][BF_4]$ in the presence of alkyne.[14,15] The structure of this complex has now been determined.[16]

In attempts to prepare the elusive species "$Ru_3(\mu\text{-}RCCR')(CO)_9$",[6a,17] we have carried out the reaction of $[PPN][Ru_3(\mu\text{-}Cl)(\mu\text{-}RCCR')(CO)_9]$ with protic solvents in the absence of ligand. In the case of phenylacetylene (reaction 3), immediate precipitation of the known[18] acetylide species $[PPN][Ru_3(\mu_3\text{-}CC(C_6H_5))(CO)_9]$ ([PPN][**8b**]) is observed.[19]



[PPN][4b] [PPN][8b] (3)

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 known[20] neutral dihydrido species $Ru_3(\mu\text{-}H)_2(\mu\text{-}RCCR')(CO)_9$ (**9b–d**) within 15–20 min.[21]



[PPN][4b-d] (9b-d) (4)

The neutral complex **9** is not seen when reaction 4 is carried out in THF; instead, the complexes $[PPN][Ru_3(\mu\text{-}H)(\mu\text{-}RCCR')(CO)_9]$ ([PPN][**10**]), $[PPN][HRu_3(CO)_{11}]$, and $[PPN][H_3Ru_4(CO)_{12}]$ 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 $[PPN][BH_4]$ in THF (100% spectroscopic yield), and (iv) direct reaction of an alkyne with $[HRu_3(CO)_{11}]^-$ (THF, 25 °C, 4 h, 40–50% yield).[21] An X-ray structure analysis of $[PPN][Ru_3(\mu\text{-}H)(\mu_3\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][**10c**])[22] reveals that the alkyne is coordinated in a $\mu_3\eta^2$-‖ 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/CH_3CN,[7] with the additional advantage that enhanced activity toward hydrogen is also observed, parallel to the behavior of related activated cluster complexes.[23,24]

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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.

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(14) $Ru_3(\mu\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (**7c**):[5a] IR (ν_{CO} (cm^{-1}), CH_2Cl_2) 2077s, 2047 vs, 2022 vs, 1990 m, 1962 m.

(15) (a) Ros, R.; Scrivanti, A.; Albano, V. G.; Braga, D.; Garlashelli, L. *J. Chem. Soc., Dalton Trans.* **1986**, 2411–2421. (b) Ros, R.; Scrivanti, 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, *C*2/*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) Å^3, *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.

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(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; ^{1}H NMR ($CDCl_3$) 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; ^{1}H NMR ($CDCl_3$) δ −19.0 (s, 1 H, hydride).

(22) Crystal data for [PPN}[**10c**}: fw = 1273.14, triclinic $P\bar{1}$, 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 Å^3, *Z* = 2, μ(Mo Kα) = 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.

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

(24) In our hands, $[PPN][Ru_3(\mu\text{-}H)(CO)_{11}]$ is quantitatively obtained by reaction of $[PPN][Ru_3(\eta^1\text{-}Cl)(CO)_{11}]$ ([PPN][**2**]) with H_2 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 ionization[1] of iodine vapor leads to the formation of $I_2^{\bullet+}(g)$. A Fourier transform ion cyclotron resonance spectrometry (FTICR)[3] study of the reactivity of this ion[4] has revealed the existence of new gas-phase ion–molecule reactions, the most important being as follows: (1) the displacement of $I^\bullet$ by n-donor bases (B), reaction 1,

$$B + I_2^{\bullet+} \rightarrow (B\text{-}I)^+ + I^\bullet \qquad (1)$$

this process generally being followed by the formation of clusters, $(B)_nI^+$;[5] (2) the exchange of iodine cation between different bases (B_1, B_2), reaction 2,

$$B_1I^+ + B_2 \overset{\delta\Delta G^\circ_{I^+}}{\rightleftharpoons} B_2I^+ + B_1 \qquad (2)$$

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 I_2 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 Brucker 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 Py_2I^+ (Poskin, G.; Huyskens, P. *Bull. Soc. Chim. Fr.* **1976**, 337 and references therein).

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