Poutsma, R. R. Squires, *Int. J. Mass Spectrom. Ion Processes* **1994**, *130*, 89–105.

[28] Flowing-afterglow or SIFT-FA mass spectrometers are commercially not available.

[29] F. Cacace, *Acc. Chem. Res.* **1988**, *21*, 215–222.

[30] Reviews: a) M. Speranza, *Mass Spectrom. Rev.* **1992**, *11*, 73–117; b) S. Fornarini, *Mass Spectrom. Rev.* **1996**, *15*, 365–389.

[31] For a review on the gas-phase ion chemistry of protonated benzene and of protonated alkylbenzenes, see D. Kuck, *Mass Spectrom. Rev.* **1990**, *9*, 583–630.

[32] a) S. Sieber, P. von R. Schleyer, J. Gauss, *J. Am. Chem. Soc.* **1993**, *115*, 6987–6988; b) M. N. Glukhovtsev, A. Pross, A. Nicolaides, L. Radom, *J. Chem. Soc. Chem. Commun.* **1995**, 2347–2348; c) E. del Rio, R. López, T. L. Sordo, *J. Phys. Chem. A* **1997**, *101*, 10090–10094.

[33] For more recent work on the chemistry of protonated alkylbenzenes, see a) D. Kuck, *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 441–455; b) F. Cacace, M. E. Crestoni, S. Fornarini, D. Kuck, *J. Am. Chem. Soc.* **1993**, *115*, 1024–1031; c) S. T. Howard, K. Woźniak, *Chem. Phys. Lett.* **1993**, *212*, 1–4; d) R. S. Mason, C. M. Williams, P. D. J. Anderson, *J. Chem. Soc. Chem. Commun.* **1995**, 1027–1028; e) T. Xu, D. H. Barich, P. D. Torres, J. F. Haw, *J. Am. Chem. Soc.* **1997**, *119*, 406–414; f) D. Kuck, A. Petersen, U. Fastabend, *Int. J. Mass Spectrom. Ion Processes* **1998**, *179/180*, 129–146; g) D. Kuck, U. Fastabend, *Int. J. Mass Spectrom. Ion Processes* **1998**, *179/180*, 147–163; h) M. Tanaka, M. Fujiwara, Q. Xu, H. Ando, T. J. Raeker, *J. Org. Chem.* **1998**, *63*, 4408–4412; i) P. C. Miklis, R. Ditchfield, T. A. Spencer, *J. Am. Chem. Soc.* **1998**, *120*, 10482–10489; j) G. Bouchoux, M. Yáñez, O. Mó, *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 241–251; k) M. Mormann, D. Kuck, *J. Mass Spectrom.* **1999**, *34*, 384–394.

[34] F. Cacace, M. E. Crestoni, S. Fornarini, *J. Am. Chem. Soc.* **1992**, *114*, 6776–6784.

[35] a) B. Chiavarino, M. E. Crestoni, C. H. DePuy, S. Fornarini, R. Gareyev, *J. Phys. Chem.* **1996**, *100*, 16201–16208; b) C. H. DePuy, R. Gareyev, S. Fornarini, *Int. J. Mass Spectrom. Ion Processes* **1997**, *151*, 41–45; c) S. Fornarini, M. E. Crestoni, *Acc. Chem. Res.* **1998**, *31*, 827–834.

[36] a) G. A. Olah, R. H. Schlosberg, D. P. Kelly, G. D. Mateescu, *J. Am. Chem. Soc.* **1970**, *92*, 2546–2548; b) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, G. D. Mateescu, *J. Am. Chem. Soc.* **1972**, *94*, 2034–2043; c) G. A. Olah, J. S. Staral, G. Ascensio, G. Liang, D. A. Forsyth, G. D. Mateescu, *J. Am. Chem. Soc.* **1978**, *100*, 6299–6308.

[37] For applications of FT-ICR mass spectrometry in organic chemistry, see J. S. Pyrek, *Synlett* **1999**, 249–266.

[38] M. Schlosser, J. Porwisiak, F. Mongin, *Tetrahedron* **1998**, *54*, 895–900.

[39] M. Schlosser, F. Mongin, J. Porwisiak, W. Dmowski, H.-H. Büker, N. M. M. Nibbering, *Chem. Eur. J.* **1998**, *4*, 1281–1286.

[40] J. L. Devlin, III, J. F. Wolf, R. W. Taft, W. J. Hehre, *J. Am. Chem. Soc.* **1976**, *98*, 1990–1992.

[41] G. I. Mackay, R. S. Hemsworth, D. K. Bohme, *Can. J. Chem.* **1976**, *54*, 1624–1642.

[42] a) S. Ingemann, N. M. M. Nibbering, *J. Chem. Soc. Perkin Trans. 2* **1985**, 837–840; b) See also J. J. Grabowski, P. D. Roy, R. Leone, *J. Chem. Soc. Perkin Trans. 2* **1988**, 1627–1632.

[43] a) J. B. Cummings, P. Kebarle, *Can. J. Chem.* **1978**, *56*, 1–9; b) J. E. Bartmess, J. A. Scott, R. T. McIver, Jr., *J. Am. Chem. Soc.* **1979**, *101*, 6046–6056.

[44] a) M. Eckert-Maksić, M. Klessinger, Z. B. Maksić, *J. Phys. Org. Chem.* **1995**, *8*, 435–441; b) M. Eckert-Maksić, M. Klessinger, Z. B. Maksić, *Chem. Eur. J.* **1996**, *2*, 1251–1257; c) Z. B. Maksić, B. Kovačević, D. Kovaček, *J. Phys. Chem. A* **1997**, *101*, 7446–7453.

“Simple” Carbonyls of Ruthenium: New Avenues from the Hieber Base Reaction

Anthony F. Hill*

The rush to develop increasingly more complex and sophisticated transition metal catalysts by ingenious coligand design continues to gather momentum. In this climate it is both refreshing and sobering when results of substantial scientific significance emerge from studies of older and simpler organometallic compounds, which can effectively mediate technologically useful processes. Ultimately, the simpler the system, the more generally applicable are the lessons to be learnt. One such system is provided by the carbonyl chlorides of ruthenium(II), which arise from the carbonylation of alcoholic solutions of commercially available hydrated ruthenium chloride “$RuCl_3 \cdot x H_2O$”. The resulting yellow solution, described[1a] as including “species of doubtful composition prepared in situ” finds wide use in the preparation of numerous complexes of the form $[RuCl_2(CO)_2L_2]$ (L = phosphanes, arsanes, thioethers etc).[1] Not only do such solutions provide access to the carbonyl chemistry of divalent ruthenium. Bruce and Stone first showed that zinc reduction provided the binary zerovalent carbonyl $[Ru_3(CO)_{12}]$.[2] This remains the preferred route to this compound, the subsequent chemistry of which has featured in thousands of papers.[3] This early study provided some key insights, including the isolation of dimeric $[Ru_2(\mu\text{-}Cl)_2Cl_2(CO)_6]$ (**1**) and the observation that the halide bridges were easily and reversibly cleaved by the weak nucleophile THF to provide *fac*-$[RuCl_2(thf)(CO)_3]$ (**2**). Chloride also reversibly cleaves dimeric **1**, or replaces the labile THF in **2**, to provide the ruthenate *fac*-$[RuCl_3(CO)_3]^-$ ($\mathbf{3}^-$). In the intervening 33 years, the comparative ignorance of the true nature of the interacting species involved in such alcoholic solutions has been more than excused by the enormous synthetic utility. Recent studies, primarily those of Lavigne and co-workers,[4] have however sought to understand this witches brew, driven in part by the utility of carbonyl halide complexes of divalent ruthenium in various catalytic processes. Amongst these is the water–gas shift

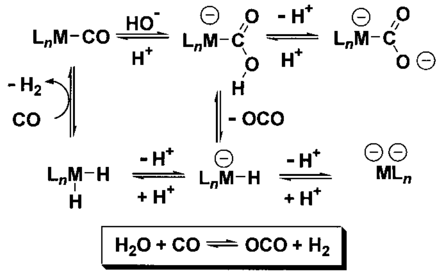
---

[*] Dr. A. F. Hill
Centre for Chemical Synthesis, Department of Chemistry
Imperial College of Science, Technology and Medicine
London, SW7 2AY (UK)
Fax: (+44) 2075945804
E-mail: a.hill@ic.ac.uk

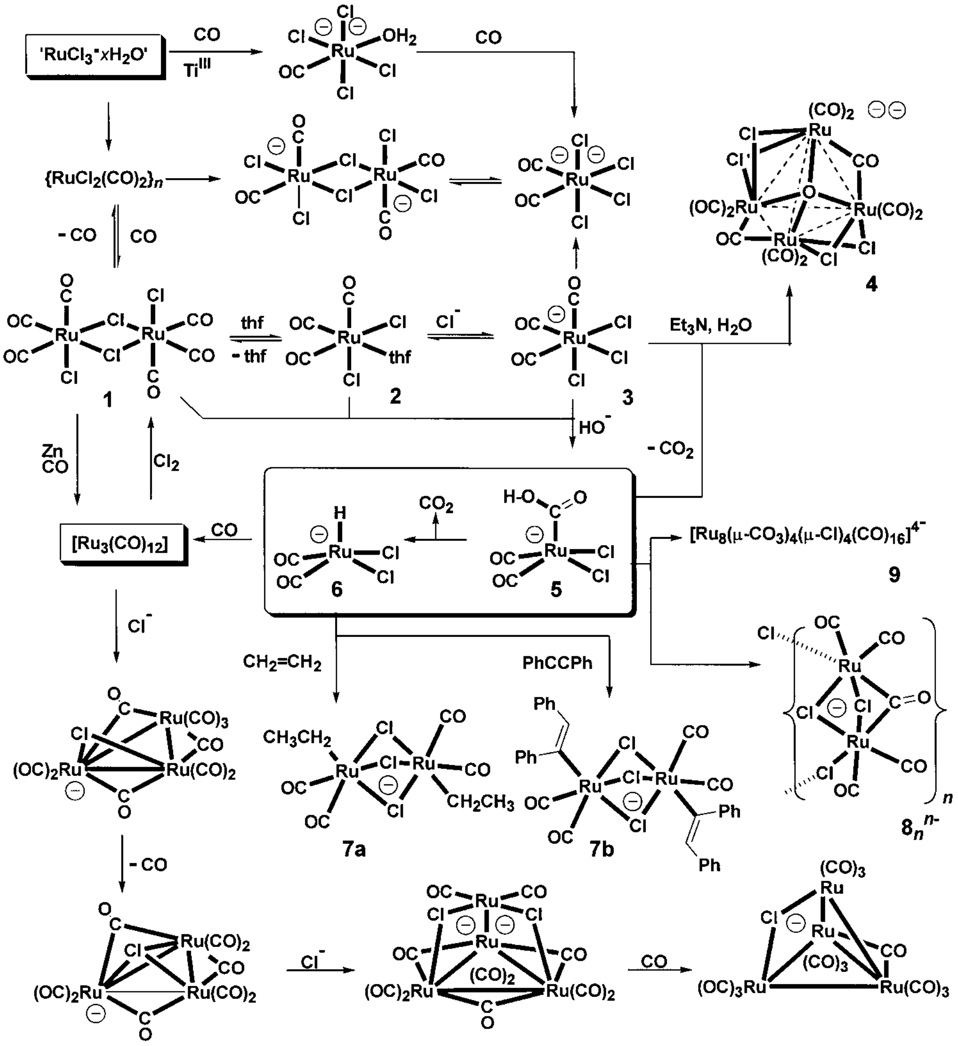
reaction, and by implication the Hieber base reaction,[5] the study of which has led to some surprising results. Herein we would like to highlight and contextualize some particularly intriguing results currently emerging.[6–8]

Scheme 1 presents a manifold of well-characterized carbonylchlororuthenium(II) species. Elsewhere can be found the specific conditions devised to favor the predominance or isolation of each species.[4, 6, 7] The important point however is that each and every one of these species might be considered to be potentially present and operative in catalytic "broths" employing carbonylated ruthenium chloride or mixtures of $[Ru_3(CO)_{12}]$ and chloride sources. Despite the complexity of this reaction manifold, the study of the individual species and their inter-relationship has been made possible by convenient and reliable routes to each of the components. In particular the carbonyl ruthenate $\mathbf{3}^-$ may be conveniently prepared as either the Cs^+[9] or $[PPN]^+$ salts ($PPN = (PPh_3)_2N$).[10] The processes that deserve special comment are however the various reactions of **1**, **2**, or [PPN]**3** with sources of hydroxide: The conditions are crucial to the progress of the reaction, for example, with water and triethylamine the μ_4-oxo cluster **4** is obtained. With KOH, however, a (possibly *solvento*-stabilized) hydroxycarbonyl intermediate $\mathbf{5}^-$ may be observed at ambient temperatures, with clear implications for the Hieber base reaction[5] and the water–gas shift reaction[11] mediated by divalent ruthenium species.[12, 13]

Hieber's "Base reaction" is a fundament of organotransition metal chemistry, having provided the archetypal metal hydrides $K[HFe(CO)_4]$ and $[H_2Fe(CO)_4]$[5] as well as the key rationale for the metal-catalyzed water–gas shift reaction (WGSR, Scheme 2):[11] Nucleophilic attack by hydroxide at a carbonyl ligand, with subsequent formation of CO_2 and a metal hydride, can in suitable situations be followed by deprotonation of the metal hydride and overall reduction of the metal center by two units. Alternatively, protonation of the hydrido complex can lead (via a dihydride) to evolution of dihydrogen. Discovered first for iron, this reaction is becoming increasingly conspicuous in the chemistry ruthenium (Scheme 3). Thus, the analogous reaction of $[Ru(CO)_5]$ with KOH (Scheme 3a) proceeds 30000 times as fast as that for $[Fe(CO)_5]$[14] despite a generally held decrease in electrophilicity associated with descending a triad. This protocol finds particularly wide application in the reduction of metal clusters (Scheme 3b)[15] to provide high nuclearity carbonylates during which CO_2 is liberated. For π-basic and coordinatively saturated metal centers devoid of strong π acids, the possibility arises that CO_2 is retained in the coordination sphere, either as a hydroxycarbonyl group or as σ-CO_2 itself (Scheme 3c)[13] Furthermore, although mechanistically divergent, the use of methoxide as the nucleophile towards CO, can also effect reduction of divalent ruthenium and osmium carbonyl compounds (Scheme 3d).[16, 17]

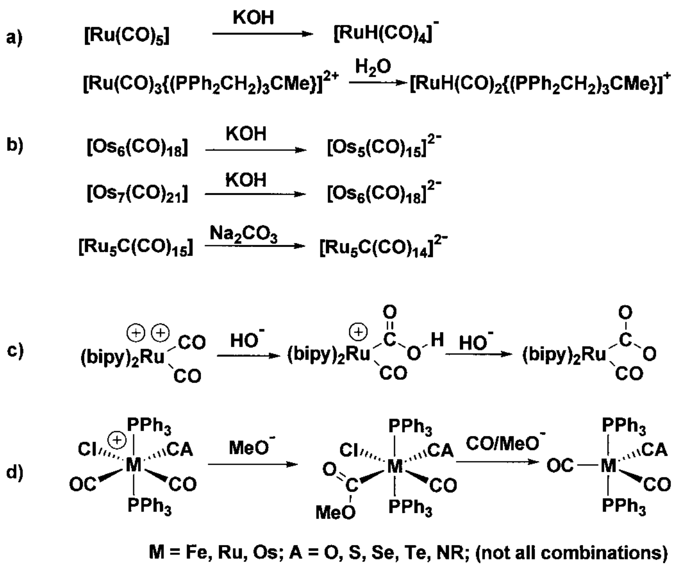


Scheme 2. Metal-mediated water–gas shift reaction (WGSR).



Scheme 1.

The hydroxycarbonyl intermediate K[**5**] slowly decarboxy-



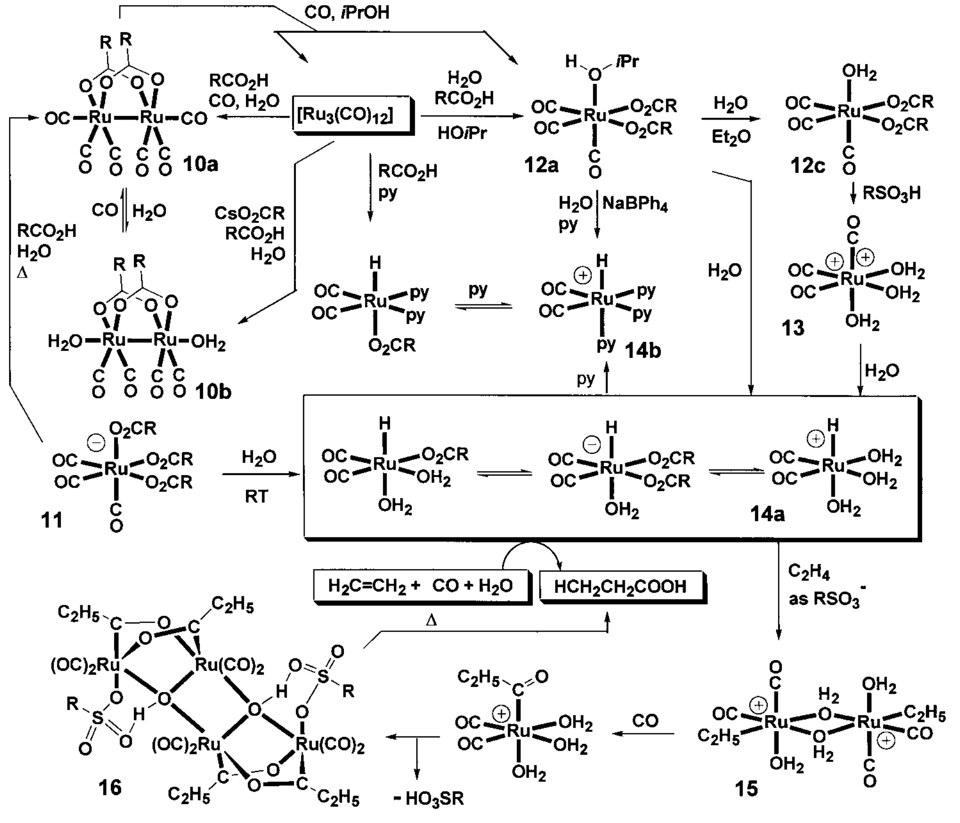
Scheme 3. Hieber base reactions with ruthenium and osmium complexes.

lates when heated to provide a putative hydrido salt K[**6**] which has so far defied isolation, due perhaps in part to its strong Brønsted acidity.[7] Attempts to trap this 16-electron (or possibly solvated or dimeric) complex by carbonylation and formation of $K[RuHCl_2(CO)_3]$ perhaps not surprisingly appears to increase the acidity and facile reductive elimination occurs to provide $[Ru_3(CO)_{12}]$ in excellent yield. Condensing all the steps from "$RuCl_3 \cdot x H_2O$" in a one-pot low-pressure procedure provides $[Ru_3(CO)_{12}]$ directly in 86% yield! The improved access to this already intensely studied compound is highly significant, obviating the use of high-pressure equipment. The assertion that a hydrido complex is indeed involved is however provided by trapping experiments with a range of unsaturated organic compounds: Heating K[**5**] in the presence of ethene or tolane provide, respectively, the dinuclear ethyl and stilbenyl complexes $[Ru_2(\mu\text{-}Cl)_3R_2(CO)_4]^-$ (R = $CH_2CH_2\mathit{H}$ **7a**, CPh=C*H*Ph **7b**) (Scheme 1) which serve as synthetic equivalents in situ for "$RuCl(CO)_2R$" in reactions with added ligands, for example, PPh_3.[7]

In further studies on the formation of **5**, Lavigne et al. have very recently found a remarkable dependence on conditions and hydroxide source: In concentrated methanol [Et4N][OH] reacts with **2** to provide the polymeric species $\{[Et_4N][Ru_2(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_4](\mu\text{-}Cl)\}_n$. ($[Et_4N]$[**8**]) The repeat unit of this polymer might be described as a Ru^I-Ru^I core given that the unique chloro ligand lies equidistant between adjacent diruthenium cores. However, an alternative mixed-valence $[Ru^{II}-Ru^0]$ description also has instructional merit, that is, one can view the polymer as arising from combination of **3** and "$Ru(CO)_2$". Indeed, if the reaction is carried out under an atmosphere of CO, no **8** is observed; rather a mixture of $[Ru_3(CO)_{12}]$ and Et_4N[**3**] is obtained. The polymer degrades in acetonitrile to give what is presumed to be a solvated form of the "$Ru_2(\mu\text{-}Cl)_2(CO)_5(NCMe)_x$" anion, for which a rich chemistry may be anticipated.[8]

A second minor side product is also obtained from [Et4N]OH, **2** (and adventitious Na^+), the yield of which may be increased by the addition of $NaHCO_3$. The molecular architecture of the resulting tetraanionic cage **9** can only be described as beautiful, comprising four "$Ru_2(CO)_4$" units bridged by chloride and carbonate buttresses. The latter arises from CO_2 liberated from the hydroxycarbonyl precursor and if this is purged from the reaction mixture, the formation of **9** is suppressed in favor of the μ-oxo species **4** previously obtained from **3** and moist Et_3N.[8]

Throughout this chemistry, the role of the chloride coligands has been far from innocent, readily forming bridges in di-, oligo-, and polymeric assemblies (thereby weakly masking potential coordination sites) and as a π-donor presumably moderating the reactivity of the carbonyl ligands. A related "halide-free" chemistry has however emerged from the group of Fachinetti and Funaioli (Scheme 4, R = CF_3)[18–20] and the recurrent parallels between the two systems are noteworthy. This chemistry originates from a detailed study of the WGSR mediated by $[Ru_3(CO)_{12}]$ in acidic media (CF_3CO_2H, H_2O, diglyme). The species $[Ru_2(\mu\text{-}O_2CCF_3)_2(CO)_6]$ (**10a**) and *fac*-$[Ru(O_2CCF_3)_3(CO)_3]^-$ (**11**) underpin the WGSR catalytic manifold; however, it is their synthetic utility which perhaps



Scheme 4.

holds the most promise. In the presence of excess trifluoroacetate the former readily disproportionates into the latter and $[Ru_3(CO)_{12}]$ (recall the implicit carbonylation of **8** to provide **3** and $[Ru_3(CO)_{12}]$). Under acidic conditions, the latter reacts with water to provide $[Ru_2(\mu\text{-}O_2CCF_3)_2(CO)_4(OH_2)_2]$ (**10b**), hydrogen, and CO_2. This complex is related to the recently characterized complex $[Ru_2(\mu\text{-}O_2CCF_3)_2(CO)_4(NCMe)_2]$ (**10c**), obtained in high yield by Bruce et al. from $[Ru_3(CO)_{12}]$ and CF_3CO_2H in acetonitrile.[21] In acid-free THF, the reaction with water appears to give equilibrating hydrido complexes of the form $[RuH(CO)_2(O_2CCF_3)_nL_{4-n}]^{1-n}$ (L = THF, H_2O). For $n = 1$, thermolysis provides **10b** and hydrogen. A useful substrate to emerge from this work is the complex $[Ru(O_2CCF_3)_2(CO)_3(i\text{PrOH})]$ (**12a**). Although the thf ligand in $[Ru(O_2CCF_3)_2(CO)_3(thf)]$ (**12b**) (obtained by carbonylation of $[Ru_2(\mu\text{-}O_2CCF_3)_4(thf)_2]$) is less labile than that of **2**,[22] the *i*PrOH ligand in **12a** is readily replaced by water to provide the complex $[Ru(O_2CCF_3)_2(CO)_3(OH_2)]$ (**12c**) simply on recrystallization from moist diethyl ether. This species provides the entry point for a wealth of chemistry of water-soluble organoruthenium compounds, for example, dissolution in acidified (HOTf) water provides the dicationic complex $[Ru(CO)_3(OH_2)_3]^{2+}$ (**13**). At higher pH however the carbonyl ligands of this complex are readily attacked by water to provide the hydrido salt *fac*-$[RuH(CO)_2(OH_2)_3]$OTf ([**14a**]OTf). As with **4**, **14a** hydrometalates ethene to provide an ethyl derivative; however, in this case water rather than chloride bridges support the adopted dinuclear structure **15**. Carbonylation of **15** results in migratory insertion and formation of the propionoyl-bridged complex **16** with coordinated triflate ligands. The tetranuclear assembly is held together by μ_3-hydroxide bridges, which are intramolecularly hydrogen-bonded to triflate ligands. At high temperatures, however, the propionoyl complex generates propionic acid in a catalytic cycle from ethene, CO, water, and hydrogen, which is also mediated by **14a**. The involvement of such thermally robust and acid-stable hydrido, alkyl, and acyl complexes in this system is most impressive.

Further work: From the above it is clear that much has been learnt and remains to be learnt from the study of the "simple" carbonyls of divalent ruthenium, however further directions also present themselves. Kinetic studies on the reactions of KOH with the zerovalent pentacarbonyl complexes $[M(CO)_5]$ show rates increasing in the order $M = Fe \ll Ru < Os$.[14] This trend might reasonably be expected to carry through to the chemistry of the divalent state and therefore make the chemistry of osmium carbonyl chlorides particular attractive, especially in catalytic applications. Unfortunately at present the synthetic routes to species such as $[Os_2(\mu\text{-}Cl)_2Cl_2(CO)_6]$ remain far less convenient[23] than those developed in the ruthenium system. The report of a multi-gram high-yield (83 %) synthesis from silica-supported osmium chloride is however encouraging.[24] Other anionic coligands are also of interest. Parallels have emerged between the chemistries of Lavigne's chloride and Fachinetti's trifluoroacetate systems, although at first sight these ligands would appear to have little in common. The former is soft and π-basic, the latter hard, and yet similar key transformations have been effected. It would therefore seem that there is much scope for coligand variation. Perhaps most timely in this respect is the preparation of carbonyl fluorides, for example, $[Ru_2(\mu\text{-}F)_2F_2(CO)_6]$ reported by Holloway and Hope.[25] The potential π and/or Brønsted basicity of coordinated fluoride in such systems offers considerable intrigue (in appropriate solvent systems), perhaps offering a compromise between the properties of chloride and trifluoroacetate ligands. These comments on diversification however in no way distract from the rich organometallic chemistry, which will continue to emerge from the (not so) simple chloro-and trifluoroacetato carbonylruthenium(II) complexes.

---

[1] M. A. Bennett, M. I. Bruce, T. W. Matheson in *Comprehensive Organometallic Chemistry, Vol. 4* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**, pp. 692–694; J. P. Collman, W. R. Roper, *J. Am. Chem. Soc.* **1965**, *87*, 4008.

[2] M. I. Bruce, F. G. A. Stone, *J. Chem. Soc. A* **1967**, 1238.

[3] A. F. Hill, A. J. Deeming, R. K. Pomeroy, M. P. Cifuentes, M. G. Humphrey in *Comprehensive Organometallic Chemistry II, Vol. 7* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1995**.

[4] G. Lavigne, *Eur. J. Inorg. Chem.* **1999**, 917.

[5] W. Hieber, E. Becker, *Chem. Ber.* **1930**, *63*, 1405; W. Hieber, H. Vetter *Chem. Ber.* **1931**, *64*, 2340.

[6] S. Fabre, P. Kalck, G. Lavigne, *Angew. Chem.* **1997**, *109*, 1167; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1092.

[7] M. Faure, L. Maurette, B. Donnadieu, G. Lavigne, *Angew. Chem.* **1999**, *111*, 539; *Angew. Chem. Int. Ed.* **1999**, *38*, 518.

[8] L. Maurette, B. Donnnadieu, G. Lavigne, *Angew. Chem.* **1999**, *111*, 3919; *Angew. Chem. Int. Ed.* **1999**, *38*, 3707.

[9] M. J. Cleare, W. P. Griffith, *J. Chem. Soc. A* **1969**, 372.

[10] N. Lugan, G. Lavigne, J. M. Soulie, S. Fabre, P. Kalck, J. Y. Saillard, J. F. Halet, *Organometallics* **1995**, *14*, 1712.

[11] P. C. Ford, *Acc. Chem. Res.* **1981**, *14*, 31; P. C. Ford, A. Rokicki, *Adv. Organomet. Chem.* **1988**, *28*, 139.

[12] D. Choudhury, D. J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.* **1982**, 1855; D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1980**, 1213.

[13] H. Tanaka, H. Nagao, S.-M. Peng, K. Tanaka, *Organometallics* **1992**, *11*, 1450.

[14] D. C. Gross, F. C. Ford, *Inorg. Chem.* **1982**, *21*, 1703.

[15] G. R. John, B. F. G. Johnson, J. Lewis, *J. Organomet. Chem.* **1979**, *169*, C9; A. G. Cowie, B. F. G. Johnson, J. Lewis, P. R. Raithby, *J. Organomet. Chem.* **1986**, *306*, C63.

[16] W. Hieber, V. Frey, P. John, *Chem. Ber.* **1967**, *101*, 1961.

[17] K. R. Grundy, W. R. Roper, *J. Organomet. Chem.* **1976**, *113*, C45; W. R. Roper, *J. Organomet. Chem.* **1986**, *300*, 167.

[18] G. Fachinetti, T. Funaioli, F. Marchetti, *J. Organomet. Chem.* **1995**, *498*, C20.

[19] G. Fachinetti, T. Funaioli, L. Lecci, F. Marchetti, *Inorg. Chem.* **1996**, *35*, 7217.

[20] T. Funaioli, C. Cavazza, F. Marchetti, G. Fachinetti, *Inorg. Chem.* **1999**, *38*, 3361.

[21] M. I. Bruce, B. W. Skelton, A. H. White, N. N. Zaitseva, *Aus. J. Chem.* **1999**, *52*, 621.

[22] A. J. Lindsay, G. Wilkinson, M. Motevalli, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1987**, 2723.

[23] L. A. W. Hales, R. J. Irving, *J. Chem. Soc. A* **1967**, 1932; W. A. Herrmann, E. Herdtweck, A. Schaefer, *Chem. Ber.* **1988**, *121*, 1907; W. Hieber, H. Stallmann, *Chem. Ber.* **1942**, *75*, 1472; R. Psaro, C. Dossi, *Inorg. Chim. Acta* **1983**, *77*, L255.

[24] D. Roberto, R. Psaro, R. Ugo, *Organometallics* **1993**, *12*, 2292.

[25] K. S. Coleman, J. H. Holloway, E. G. Hope, *J. Chem. Soc. Dalton Trans.* **1997**, 1713.