The tandem benzannulation/nucleophilic aromatic addition permits synthetic strategies for direct access to either spirobicyclic or fused bicyclic intermediates. It also obviates many of the tactical problems that have been encountered previously in the intramolecular application of aromatic nucleophilic additions to chromium arene complexes, which may be transferable to intermolecular examples as well.

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Supplementary Material Available: Spectral data for all new compounds and general procedures for the benzannulation and aromatic nucleophilic substitution reactions and the preparation of **10b** (11 pages). Ordering information is given on any current masthead page.

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New Polymetallic Ruthenium Carbonyl Halide Complexes: Exotic Combinations of Electron Deficient Skeletons with Electron Rich Anions. Their Potential Interest in Ethylene Hydroesterification

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In connection with the observation that mixtures of $Ru_3(CO)_{12}$ and [PPN]Cl are good catalyst precursors in the hydroesterification of ethylene by methyl formate[1] to produce methyl propionate (eq 1),[2,3] we attempted to trace the transformation of preformed ruthenium carbonyl halide species $[PPN][Ru_3(Cl)(CO)_{12-n}]$ (**1–3**) ($n = 1, 2, 3$)[4–6] under catalytic conditions.

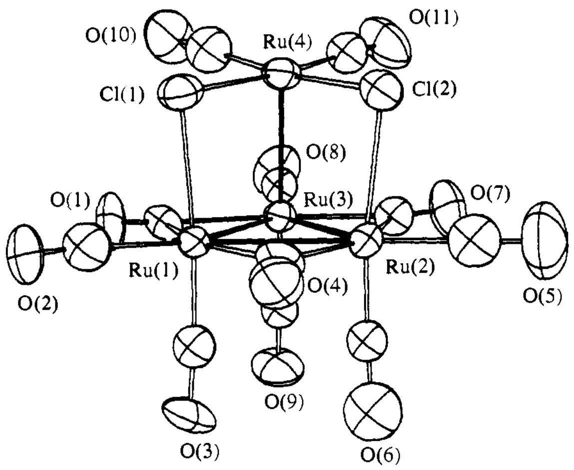

Figure 1. Perspective view of the dianionic unit of complex **4**. Selected interatomic distances (Å): Ru(1)–Ru(3) = 2.812 (2); Ru(2)–Ru(3) = 2.806 (2); Ru(1)–Ru(2) = 2.870 (1); Ru(3)–Ru(4) = 2.766 (2); Ru(1)···Ru(4) = 3.502 (2); Ru(2)···Ru(4) = 3.463 (2); Ru(1)–Cl(1) = 2.536 (4); Ru(2)–Cl(2) = 2.534 (4); Ru(4)–Cl(1) = 2.417 (4); Ru(4)–Cl(2) = 2.416 (4).

$$H_2C{=}CH_2 + HC(O)OCH_3 \xrightarrow[\text{160 °C, 12 h, 100\% conversion}]{\text{Ru}_3\text{(CO)}_{12}\text{/1PPN]Cl, dimethylformamide}} \underset{\text{99\% selectivity, turnover = 339}}{CH_3CH_2C(O)OCH_3} \quad (1)$$

During the course of preliminary experiments aimed at evaluating the optimum Ru/halide ratio, we were led to discover that $[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]$ (**3**)[5h] reacts cleanly with [PPN]Cl under a stream of inert gas to provide a unique dianionic species $[PPN]_2[Ru_4(\mu\text{-}Cl)_2(CO)_{11}]$ (**4**) according to eq 2.[3]

$$\underset{\mathbf{3}}{4[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]} + 2[PPN]Cl \xrightarrow[\text{THF, 60 °C, 1 h}]{\text{argon stream}} \underset{\mathbf{4}}{3[PPN]_2[Ru_4(\mu\text{-}Cl)_2(CO)_{11}]} + 3CO \quad (2)$$

The red complex **4**, insoluble in THF, was isolated by filtration, recrystallized in 70% yield, and characterized by X-ray analysis.[3,7]

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(2) Catalytic runs performed in a 100-mL autoclave; HCOOMe, 0.081 mol; DMF, 15 mL; ethylene, 20 bar (at 25 °C); $T = 160$ °C; time = 12 h. Catalyst precursor: $Ru_3(CO)_{12}$/[PPN]Cl (1/1); substrate/catalyst molar ratio, 345. Turnover = 339 (moles of formate converted per mole of catalyst). The only side product is 3-pentanone (<1%).[3]

(3) Full details and provided in the supplementary material.

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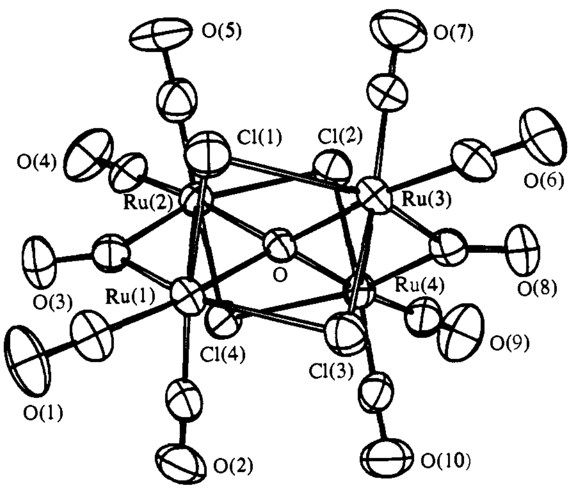

Figure 2. Perspective view of the dianionic unit of complex **6**. Selected interatomic distances (Å): Ru(1)–Ru(2) = 3.063 (1); Ru(3)–Ru(4) = 3.057 (1); Ru(1)···Ru(3) = 3.262 (1); Ru(3)···Ru(4) = 3.199 (1); Ru(1)–O = 2.080 (5); Ru(3)–O = 2.078 (4); Ru(2)–O = 2.084 (4); Ru(4)–O = 2.079 (4); Ru(1)–Cl(1) = 2.459 (2); Ru(3)–Cl(3) = 2.449 (2); Ru(2)–Cl(4) = 2.463 (2); Ru(4)–Cl(2) = 2.474 (2); Ru(1)–Cl(3) = 2.702 (2); Ru(3)–Cl(1) = 2.836 (2); Ru(2)–Cl(2) = 2.678 (2); Ru(4)–Cl(4) = 2.649 (2).

Its dianionic tetranuclear unit (Figure 1) consists of a basic triangular metal framework "$Ru_3(CO)_9$" one face of which is supported by a spiked "$Ru(CO)_2Cl_2$" fragment. The most striking feature is indeed the occurrence of a square pyramidal geometry about the 16e metal center Ru(4) [with Ru(3) as the apical atom]. In the rare cases where such a geometry is found,[8-10] the vacant octahedral site is generally protected by an agostic interaction,[11] as exemplified by $RuCl_2(PPh_3)_3$ (Ru···H = 2.59 Å).[9] The shortest intermolecular contact in **4** involves Ru(4) and an H atom belonging to a PPN cation [Ru(4)···H(53) = 2.919 (9) Å]. Extended Hückel MO calculations[12,13] indicate a large HOMO/LUMO gap (1.45 eV).[3]

As expected due to its unsaturation, the compound is highly reactive. Fast reaction with CO at 25 °C induces loss of one halide, thus yielding $[PPN][Ru_4(\mu\text{-}Cl)(CO)_{13}]$ (**5**).[5d,14]

Solutions of complex **4** rapidly turn yellow upon exposure to air. Further recrystallization from acetone/ethanol provides bright yellow crystals (22% yield) of a new compound, formulated as $[PPN]_2[Ru_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4(CO)_{10}]$ (**6**) on the basis of an X-ray analysis.[3,15] The structure of its dianionic molecular unit (Figure 2) consists of a distorted quadratic antiprism (D_2 symmetry) based on two square faces $Ru(\mu\text{-}Cl)_2Ru$ and containing an encapsulated oxygen atom linked to the four ruthenium centers.[16] Each ruthenium center of one face is connected with an equivalent one of the opposite face through a CO-bridged metal–metal bond. The halide bridges are asymmetric.

Complex **4** was found to act as a good catalyst precursor[17] in the hydroesterification of ethylene by methyl formate, a reaction discovered some years ago by Sneeden and co-workers,[18] and also investigated by Keim et al.[19] A highly efficient process based on $RuCl_3$/iodide has been patented recently.[20]

The catalyst precursors used in our preliminary approach were preformed anionic ruthenium complexes involving hydrido, alkoxy (pyridonate), amido (anilinopyridyl),[21] acetate, and halide ligands associated with various cations.[3] Though poorly active in THF, they all became moderately efficient when dimethylformamide was used as a solvent.[3,22] The best performances were recorded with chloride complexes associated with PPN cation, at 160 °C.[3] A net loss of selectivity (production of methanol and CO) was observed at higher temperatures. This was found to be consistent with an earlier report that $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ exhibits low activity at 230 °C, the temperature at which the unpromoted cluster $Ru_3(CO)_{12}$ appeared to be the best precursor.[19]

Regardless of the composition and structure of the preformed anionic ruthenium catalyst precursor, the principal metal-containing species recovered at the end of catalytic runs was identified as the known complex $[PPN]_2[Ru_6(C)(CO)_{16}]$ (**7**).[23] Yet, using **7** as a precursor resulted in moderate activity and low selectivity (53% conversion, 44% selectivity). Since the latter dianion had been previously identified as the final metal-containing species in the Ru/iodide system developed by Dombek for the conversion of syngas to ethylene glycol, we also tested mixtures of $[PPN][Ru_3(\mu\text{-}H)(CO)_{11}]$ and $[PPN][Ru(CO)_3Cl_3]$[24] as catalyst precursors for the hydroesterification reaction. *This resulted in a spectacular rate enhancement and completion of the reaction within 90 min. Finally, we next found that only* $[PPN][Ru(CO)_3Cl_3]$ *is required.*[3] The performances of this formate-based catalytic system are presently matching those of the relevant alkoxy-carbonylation process (CO + MeOH) reported by Hidai et al.[25] Though the active species is still unknown, there is growing evidence that it can be generated from a variety of anionic precursors. The important lability of ruthenium carbonyl halide aggregates highlighted in the present work may provide the clue to their efficiency in this catalytic system.

Acknowledgment. We thank the CNRS for financial support. One of us (O.L.) thanks ATOCHEM for a research grant.

Supplementary Material Available: Experimental details for preparation and characterization of the complexes, catalytic reactions, and theoretical calculations and tables of crystallographic data including listing of atomic coordinates, anisotropic thermal parameters, selected interatomic distances, and bond angles (24 pages); listing of observed and calculated structure factor amplitudes for **4** and **6** (64 pages). Ordering information is given on any current masthead page.

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(7) (a) Spectroscopic data for **4**: IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 2015 (m), 1971 (vs), 1960 (s, sh), 1919 (mw), 1895 (s), 1770 (ms, br). (b) Crystal data for **4** (crystallizes with 1.5 mol of CH_2Cl_2 per unit cell): triclinic $P\bar{1}$, No. 2, a = 18.209 (2) Å, b = 18.877 (3) Å, c = 13.895 (2) Å, α = 110.70 (1)°, β = 108.43 (1)°, γ = 87.43 (1)°, V = 4226 (1) Å^3, Z = 2, R = 0.053, R_w = 0.068 for 5493 reflections and 508 variables.

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(15) (a) Spectroscopic data for **6**: IR (ν_{CO}, cm^{-1}, CH_2Cl_2) 2011 (vs), 1938 (vs), 1710 (m, br). (b) Crystal data for **6**: triclinic $P\bar{1}$, No. 2, a = 13.226 (5) Å, b = 25.533 (2) Å, c = 12.771 (3) Å, α = 92.39 (1)°, β = 114.77 (3)°, γ = 85.92 (2)°, V = 3906 (2) Å^3, Z = 2, R = 0.038, R_w = 0.045 for 7753 reflections and 460 variables.

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