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Instant “Base-Promoted” Generation of Roper’s-type Ru(0) Complexes $Ru(CO)_2(PR_3)_3$ from a Simple Carbonylchlororuthenium(II) Precursor

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Originally discovered by Warren Roper in 1972,[1] the complex $Ru(CO)_2(PPh_3)_3$ represents the archetype of reactive Ru(0) carbonyl species. Due to a facile dissociative loss of one phosphine, it rapidly adds H_2, alkynes, olefins, and a variety of other substrates, thus providing a convenient entry into the chemistry of ruthenium.[2,3] Significantly, Hiraki and co-workers[4] noted its in situ generation during the course of a catalytic C−H/olefin coupling (the Murai reaction[5]) using $Ru(H)_2(CO)(PR_3)_3$ as the catalyst precursor.

A limitation to an extensive use of this valuable complex as a synthetic tool has long been the relative complexity of its indirect multistep preparative procedure.[6,7] In 1997, Caulton and co-workers disclosed a more general convenient preparation based on magnesium reduction of the Ru(II) complex $Ru(CO)_2Cl_2(PPh_3)_2$ at 60 °C over 10 h in the presence of an excess of phosphine.[8] A parallel spectacular achievement was the finding that the key 16 e^- intermediate $Ru(CO)_2(PR_3)_2$ can even be isolated in the case of certain strongly basic and bulky phosphines.[9]

We are now proposing the “user-friendly” single-step preparation of Roper’s complex displayed in Figure 1, corresponding to the simple chemical eq 1, where an efficient reduction of Ru(II) to Ru(0) is seen to take place much faster than with Mg and at milder conditions, thus raising intriguing questions of fundamental relevance.

$$Ru(CO)_3Cl_2(solv) + 4\ NEt_4OH + 3\ PR_3 \rightarrow \\ Ru(CO)_2(PR_3)_3 + [NEt_4]_2CO_3 + 2\ NEt_4Cl + 2\ H_2O \quad (1)$$

A preliminary ligand screening indicated that, with the exception of the bulky PCy_3 (only $Ru(CO)_3(PCy_3)_2$ is obtained in that case), the method applies to a broad range of phosphines, exemplified here by PPh_3, PPh_2Me, $PnBu_3$, or to desired combinations of different phosphines (vide infra). Solvents, such as ethanol[11] or acetonitrile, from which the incipient neutral complex readily precipitates, represent the best choice because, in most cases, they ensure both separation and protection of this highly reactive species. In a few cases, where the final complex is obtained as an oil, as for $Ru(CO)_2(PnBu_3)_3$, it can be readily obtained by a tandem synthesis/extraction procedure from a biphasic methanol/hexane mixture.

The three elementary steps of the reaction can be reasonably understood in terms of the proposed sequence shown in Scheme 1, reminiscent of an earlier report by Tanaka[12] that the reaction of $[Ru(bpy)_2(CO)_2][PF_6]_2$ with 2 equiv of $[NBu_4]OH$ gives an isolable η^1-CO_2 complex, $[Ru(bpy)_2(CO)(CO_2)]$.

This involves (a) instantaneous formation of a hydroxyl−carbonyl adduct $[NEt_4][Ru(CO)_2\{C(O)OH\}Cl_2(solv)]$, $[\mathbf{A}]^-$,[10b] by attachment of OH^- to the electrophilic carbon of a carbonyl ligand of $Ru(CO)_3Cl_2(thf)$; (b) displacement of the coordinated solvent by one molecule of the incoming phosphine, with formation of the new adduct $[NEt_4][Ru(CO)_2\{C(O)OH\}Cl_2(PPh_3)]$, $[\mathbf{B}]^-$; (c) simple deprotonation of the latter by the second equivalent of OH^- (acting as a Bronsted base)[13] to give an unstable dianionic CO_2 complex $[NEt_4]_2[Ru(CO)_2\{C(O)O\}Cl_2(PPh_3)]$, $[\mathbf{C}]^{2-}$. Here, the overall oxidation of CO to CO_2 corresponds to a reduction of the metal from Ru(II) to Ru(0). Dissociative loss of CO_2 and halide ions from $[\mathbf{C}]^{2-}$ with concomitant capture of the vacant sites by the remaining 2 equiv of phosphine would account for the effective fast production of the final complex $Ru(CO)_2(PPh_3)_3$. Let us note, however, that no free CO_2 can be detected by infrared at 2338 cm^{-1}. This might be due to its immediate capture by the excess of hydroxide, given that $[NEt_4]_2[CO_3]$ is effectively recovered at the end. Alternatively, the possible mechanistic implication of a transient carbonic acid complex cannot be excluded.

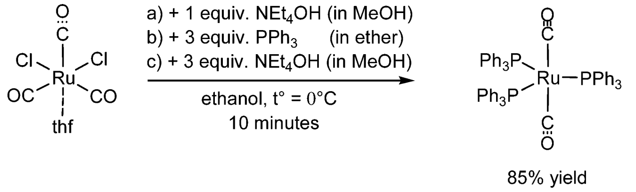
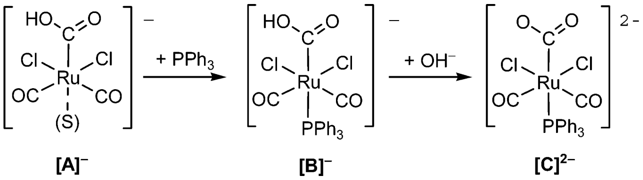


Figure 1. Preparation of $Ru(CO)_2(PPh_3)_3$: $Ru(CO)_3Cl_2(thf)$[10] (250 mg, 0.75 mmol), ethanol[11a] (5 mL). The reactants are added sequentially (but almost simultaneously over about 2 min) at ca. −5 °C: (a) 0.5 mL of NEt_4OH (1.5 M in methanol); (b) 700 mg of PPh_3 predissolved in 5 mL of ether;[11b] (c) 1.5 mL of NEt_4OH (1.5 M in methanol). Reaction is triggered by step “c” and accelerated by removal of cold bath. The complex is isolated by filtration. Of the two isomeric forms of $Ru(CO)_2(PPh_3)_3$ existing in solution, the “bis-axial” isomer shown above was identified here for the first time by X-ray diffraction (see Supporting Information).

Scheme 1. Proposed Mechanistic Pathway



The whole reaction reflects an uncommon synergism in the concerted action of OH^- and PR_3. Taken independently, none of these two reactants can achieve the reduction of the metal.

Importantly, two experimental details are crucial to the success of the reaction. First, selectivity in the production of $Ru(CO)_2(PPh_3)_3$ is achieved only if the reaction is initiated at 0 °C or below. At room temperature or above, there is unfavorable competition with a simple CO substitution leading to the well-known disubstituted derivative $Ru(CO)_2Cl_2(PPh_3)_2$ (i.e., the starting Ru(II) complex in Caulton’s method[8]) as the major contaminant. Second, the order of addition of the reactants is important. Indeed, in a preliminary separate stepwise experiment, where $Ru(CO)_3Cl_2(solv)$ was first treated with 2 equiv of NEt_4OH at 25 °C for 5 min prior to the addition of the phosphine, the initial adduct $[\mathbf{A}]^-$ was seen to add

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a second equivalent of hydroxide to give a saturated species (tentatively formulated as $[NEt_4]_2[Ru(CO)_2\{C(O)OH\}Cl_2(OH)]$, $[\mathbf{D}]^{2-}$), which then appeared to be totally reluctant to react further with the phosphine, even after hours!

So, clearly, the success of the synthesis rests on the privileged generation of the key initial adduct $[\mathbf{B}]^-$ requiring selective uptake of *one* hydroxide and *one* phosphine in the early stage of the reaction. Fortunately, such a selection is properly achieved at low temperature. Then, as an acid/base reaction, the subsequent reductive process, initiated by addition of the excess of OH^-, will be also kinetically preferred over any other transformation susceptible to occur in the coordination sphere of the metal.

Taking advantage of the stepwise ligand uptake occurring in the whole sequence, the controlled sequential incorporation of two different ligands, such as a monophosphine L1 and a diphosphine L2, is achieved with a good selectivity, as illustrated by the synthesis of $Ru(CO)_2(PPh_3)(Ph_2PN(Me)CH_2CH_2(Me)NPPh_2)$ (65% yield) where $L1 = PPh_3$ and $L2 = Ph_2PN(Me)CH_2CH_2(Me)NPPh_2$.

To date, attempts to fully separate and characterize the short-lived reactive intermediates shown in Scheme 1 remained unsuccessful. However, by reacting sequentially $Ru(CO)_3Cl_2(thf)$ with 1 equiv of NEt_4OH and 1 equiv of PPh_3 in methanol, we precipitated a crude solid whose electrospray mass spectrum showed a parent ion multiplet centered at $m/z = 557$, consistent with $[Ru(CO)_2\{C(O)O(Na)\}Cl_2(PPh_3)]^-$, $[\mathbf{C}^{2-} + \mathbf{Na}^+]^-$, an association reflecting a weakly bonding interaction between the η^1-CO_2 ligand of C^{2-} (the deprotonated form of $[\mathbf{B}]^-$) and a sodium cation, inevitably present in the spectrometer (see Supporting Information).

At first sight, the present synthetic procedure might appear as somewhat reminiscent of our recently reported synthesis of $Ru_3(CO)_{12}$.[18] Yet, attempts to replace the phosphine by a CO stream revealed that there is no way to prepare $Ru_3(CO)_{12}$ under the mild conditions used in the present experiment, thereby supporting our idea that the two reactions proceed via distinct mechanistic pathways. As previously demonstrated, the synthesis of $Ru_3(CO)_{12}$ at 75 °C involves the formation of a trappable polymeric Ru(I) complex, which undergoes CO-induced disproportionation to Ru(0) (isolated as $Ru_3(CO)_{12}$) and Ru(II) (identified as $[Ru(CO)_3Cl_3]^-$), the latter being automatically recycled upon reaction with a second equivalent of hydroxide. By contrast, the novelty of the reaction reported here rests on the unprecedented observation of an apparently direct reduction of Ru(II) to Ru(0) taking place with high efficiency and at unprecedented mild conditions.

Of numerous "minute" reactions which can be taken to illustrate the high reactivity of Roper's complex,[9b] we have selected a very elementary one, namely, the addition of trimethylsilyl acetylene, proceeding directly and quantitatively to the oxidative addition product $Ru(H)(CCSiMe_3)(CO)_2(PPh_3)_2$ (see Supporting Information).

In conclusion, it is hoped that, due to its attractive simplicity, the novel synthetic method disclosed here will pave the way for many variations in the design of new congeners of Roper's complex with sophisticated ligands and their application to a number of catalytic reactions,[5,19] where undefined mixtures of $Ru_3(CO)_{12}$ and phosphines are still presently used as catalyst precursors.

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Supporting Information Available: Experimental details for the preparation of the reported compounds and crystallographic data for $Ru(CO)_2(PPh_3)_3$ $Ru(CO)_2(PPh_2Me)_3$, $Ru(CO)_2(PPh_3)(Ph_2PN(Me)CH_2CH_2(Me)NPPh_2)$, and $Ru(H)(CCSiMe_3)(CO)_2(PPh_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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