Preparation, Properties, and Catalytic Activity of Fluorous Phosphine Substituted Transition Metal Carbonyl Complexes

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Horváth and Rábai introduced the concept of fluorous biphasic catalytic systems via the example of a successful catalytic transformation.[1-3] Their seminal paper described the hydroformylation of 1-decene to undecanals, Equation (1), in the presence of a rhodium(I) complex, $HRh(CO)\{P(CH_2CH_2(CF_2)_5CF_3)_3\}_3$. This liquid-liquid system

$$CH_3(CH_2)_7CH{=}CH_2 + H_2 + CO \rightarrow CH_3(CH_2)_9CHO + CH_3(CH_2)_7CH(CH_3)CHO \qquad (1)$$

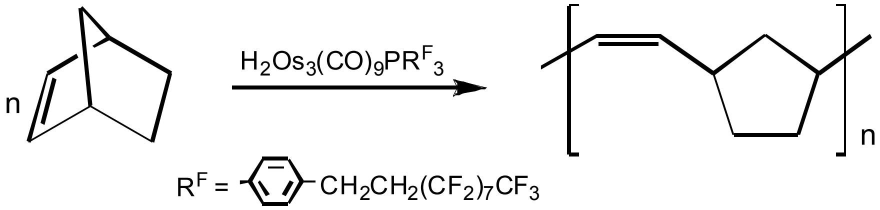
employed perfluoromethylcyclohexane and toluene as immiscible phases at room temperatures. The term *fluorous* was coined as the analog of *aqueous*, and was defined as that phase composed predominantly of fluorocarbon moieties. The perfluoroalkyl tags on the phosphine ligands imparted fluorous solubility to the rhodium complex, while the substrate was soluble in the hydrocarbon phase. The perfluoromethylcyclohexane and toluene become miscible at temperatures above 88°C.[4] Thus, the catalysis took place at elevated temperatures within a single liquid monophase. Upon cooling, the separation of the mixture into discrete hydrocarbon and fluorocarbon phases resulted in the immobilization of the rhodium(I) catalyst in the fluorous phase, while the products remained in the hydrocarbon phase.

The compounds $W(CO)_5\{P(CH_2CH_2(CF_2)_5CF_3)_3\}$, $W(CO)_5\{P(n\text{-octyl})_3\}$, and $W(CO)_5\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}$, were synthesized to probe the effects of ligation by perfluorocarbon substituted tertiary phosphines. $W(CO)_5\{P(n\text{-octyl})_3\}$ was prepared to provide a non-fluorous paradigm for $W(CO)_5\{P(CH_2CH_2(CF_2)_5CF_3)_3\}$, while $W(CO)_5PPh_3$ and $W(CO)_5\{P(o\text{-tolyl})_3\}$ were employed as standards for $W(CO)_5\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}$. The π-accepting ability of the studied phosphines was found to be $P(CH_2CH_2(CF_2)_5CF_3)_3 > P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3 > PPh_3 > P(p\text{-tolyl})_3 > P(n\text{-octyl})_3$. The X-ray crystal structure of $W(CO)_5\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}$ was determined. The electronic and structural similarity of $W(CO)_5PPh_3$ with $W(CO)_5\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}$ suggest the *para* fluorocarbon subtituents have an insignificant effect on the tungsten coordination environment.

The fluorocarbon soluble, binuclear ruthenium(I) complexes $[Ru(\mu\text{-}O_2CMe)(CO)_2L]$, where L is a perfluoroalkyl substituted tertiary phosphine, $P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3$ or $P(CH_2CH_2(CF_2)_5CF_3)_3$ were synthesized to study the catalytic hydrogenation of ketones to alcohols under fluorocarbon/hydrocarbon biphasic conditions. Catalytic hydrogenation of actophenone to 1-phenylethanol was found to occur in the presence of $[Ru(\mu\text{-}O_2CMe)(CO)_2\{P(CH_2CH_2(CF_2)_5CF_3)_3\}]_2$ or $[Ru(\mu\text{-}O_2CMe)(CO)_2\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}]_2$. Under conditions favorable to hydroformylation, the isomerization of 1-dodecene to *cis/trans*-2-dodecene arose from the presence of $[Ru(\mu\text{-}O_2CMe)(CO)_2\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}]_2$. The reactions of $[Ru(\mu\text{-}O_2CMe)(CO)_2\{P(CH_2CH_2(CF_2)_5CF_3)_3\}]_2$ and $[Ru(\mu\text{-}O_2CMe)(CO)_2\{P(p\text{-}C_6H_4\text{-}$

$CH_2CH_2(CF_2)_7CF_3)_3\}]_2$ with acetic acid were spectroscopically examined. The X-ray crystal structure of $[Ru(\mu\text{-}O_2CMe)(CO)_2\{P(CH_2CH_2(CF_2)_5CF_3)_3\}]_2$ was determined.

The triosmium carbonyl clusters $Os_3(CO)_{11}\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$ and $Os_3(CO)_{10}\{P(CH_2CH_2(CF_3)_5CF_3)_3\}_2$ were synthesized to study the behavior of transition metal carbonyl clusters in fluorocarbon phases. The reactivity of the cluster $Os_3(CO)_{11}\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$ parallels that of the parent cluster, $Os_3(CO)_{12}$: Above 100°C, PPh_3 will substitute for one or two carbonyl ligands to provide $Os_3(CO)_{10}(PPh_3)\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$ and $Os_3(CO)_9(PPh_3)_2\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$. At *ca*. 120°C and 1 atmosphere, $Os_3(CO)_{11}\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$ will activate H_2 to form the unsaturated compound $(\mu\text{-}H)_2Os_3(CO)_9\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$. At *ca*. 100°C, $Os_3(CO)_{11}\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$ will react with $HSiEt_3$ to form the mononuclear complex $HOs(SiEt_3)(CO)_3\{P(CH_2CH_2(CF_2)_5CF_3)_3\}$. The X-ray crystal structure of $Os_3(CO)_9(PPh_3)_2\{P(CH_2CH_2(CF_3)_5CF_3)_3\}$ was determined.



Polynorbornene by ring-opening metathesis polymerization was first achieved by a catalytic system of $TiCl_4$ with co-catalyst $Li[Al(n\text{-}C_7H_{15})_4]$ plus the monomer in benzene.[5] ROMP of norbornene was subsequently accomplished by employing ethanolic solutions of the monomer plus the late transition metal salts $RuCl_3\cdot 3H_2O$, $OsCl_3\cdot 3H_2O$, or $IrCl_3\cdot 3H_2O$.[6] Late transition metal catalysts are thus seen as more robust than their early transition metal counterparts, as the early transition metal systems are sensitive to oxygen and water.[7] The first industrial facility (1976) to provide commercially produced polynorbornene employed the catalytic system of $RuCl_3\cdot 3H_2O$ in *n*-butanol.[8]

Osmium complexes have been utilized in a small number of catalytic systems that provide polynorbornene by ROMP. The first such system, mentioned above, used $OsCl_3\cdot 3H_2O$ as catalyst/precursor.[6] Chronologically, OsO_4,[9] $OsH_4(PPh_3)_3$,[10] $Os(p\text{-cymene})Cl_2(PCy_3)$,[11] $Cp^*{}_2Os_2Br_4$ (and related compounds),[7] and $OsHCl(CO)(P^iPr_3)_2$[12] have been reported to possess norbornene ROMP activity. Finally, the unsaturated $46e^-$ triosmium cluster $(\mu\text{-}H)_2Os_3(CO)_{10}$ has demonstrated norbornene ROMP activity.[13]

The fluorocarbon soluble, unsaturated triosmium cluster $(\mu\text{-}H)_2Os_3(CO)_9\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}$ was prepared and characterized. Ring-opening metathesis polymerization of norbornene occurs in the presence of $(\mu\text{-}H)_2Os_3(CO)_9\{P(p\text{-}C_6H_4\text{-}CH_2CH_2(CF_2)_7CF_3)_3\}$. A number of solvent systems were employed and results were analyzed with regard to both polymer production and triosmium cluster recovery. Polymer yields of up to 107.5 kg per mole of catalyst precursor were achieved. The polynorbornene was examined primarily by ^{13}C NMR spectroscopy to determine the *cis/trans* ratio and also to determine the degree of *cis/trans* “blockiness”.[14,15]

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