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Facile Alkene Insertion into a Rhodium(III)−Acetyl Bond: Potential Catalysts for CO/Alkene Copolymerization

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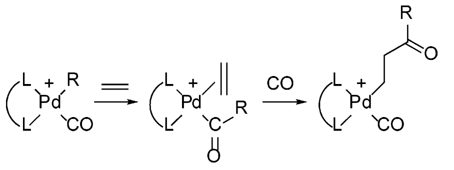
Summary: Cationic Rh(III) methyl complexes, [(η^5-ligand)Rh(CO)$_2$Me]$^+$ (η^5-ligand = C_5Me_5, C_9Me_7, $C_9Me_3H_4$), undergo facile reactions with strained alkenes (e.g. norbornadiene) to give products resulting from insertion of the alkene into a Rh−acetyl bond. Kinetic, mechanistic, and structural results are presented, along with evidence of catalytic activity for CO/alkene copolymerization.

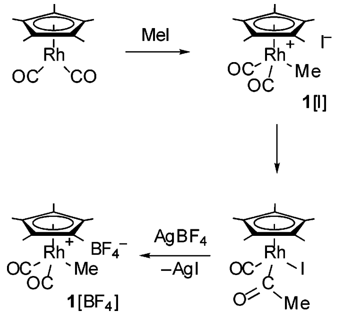
The catalytic alternating copolymerization of CO and alkenes, to give polyketones, has attracted substantial interest in recent years, from both industrial and academic researchers.[1] The process is normally achieved using Pd(II) complexes containing bidentate P,P or N,N ligands. The propagation steps, illustrated in Scheme 1, are CO insertion into a Pd−alkyl bond and alkene insertion into a Pd−acyl bond.

Other d^8 metals have also been tested as catalysts, notably Ni(II)[2] and Rh(I).[3] The Rh(I) systems, which are closely related to alkene hydroformylation catalysts, have generally resulted in formation of relatively low molecular weight co-oligomers. Migration of alkyl onto CO is often facile in d^6 Rh(III) complexes, and we sought to investigate the reactivity of such systems toward alkenes. In particular, we noted that [Cp*Rh(CO)$_2$Me]$^+$ (**1**) is proposed as a reactive intermediate in the oxidative addition of MeI to [Cp*Rh(CO)$_2$] (Scheme 2).[4] Migration of methyl onto CO in this complex would generate a vacant site cis to acetyl, ideally set up for coordination and insertion of an alkene.

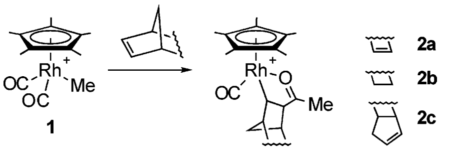
Scheme 1. Insertion Steps for Pd-Catalyzed CO/Alkene Copolymerization



Scheme 2. Formation of 1[BF$_4$]



Scheme 3. Reactions of 1 with Strained Alkenes



We found that **1**[BF$_4$] can easily be generated in solution by abstraction of iodide from [Cp*Rh(CO)(COMe)I] (Scheme 2). ^{1}H NMR evidence for **1**[OTf] has been noted previously.[5] Our NMR data for **1**[BF$_4$] are in agreement, and the IR spectrum shows ν(CO) bands at 2118 and 2087 cm^{-1}, which are 10−20 cm^{-1} higher in frequency than those of the known Ir analogue.[4]

Reaction of **1**[BF$_4$] with strained alkenes (norbornadiene (nbd), norbornene (nbe), and dicyclopentadiene) at room temperature results in the stable products **2a**−**c** (Scheme 3), which were isolated as solids and fully characterized. The IR spectra showed, in addition to the terminal ν(CO) band at ca. 2060 cm^{-1}, an acetyl ν(CO) absorption near 1620 cm^{-1}. This is significantly lower in frequency than normally found for a Rh(III) acetyl (e.g. 1685 cm^{-1} for [Cp*Rh(CO)(COMe)I]) and close to that observed for similar Pd chelates (e.g. [Pd(bipy)(κ^2-C_7H_8COMe)]$^+$).[6,7] High-frequency carbonyl ^{13}C resonances near δ 240 for **2a**−**c** provided further evidence that the carbonyl oxygen is coordinated to Rh.

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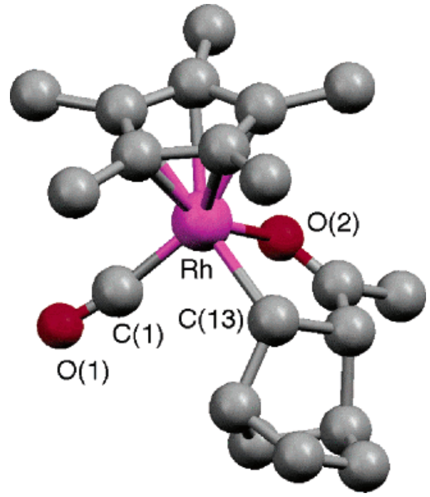
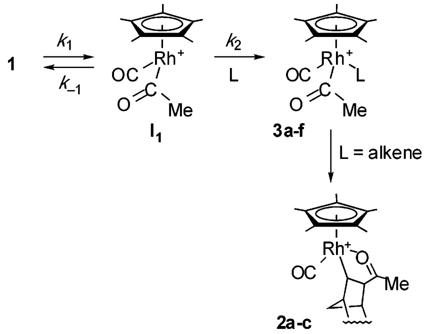


Figure 1. X-ray structure of **2a** (one of two independent molecules in the unit cell). Hydrogens and counterion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−C(1) = 1.852(12), Rh−O(2) = 2.130(5), Rh−C(13) = 2.108(9), C(1)−O(1) = 1.111(14); C(1)−Rh−C(13) = 90.7(5), O(2)−Rh−C(1) = 99.1(5), O(2)−Rh−C(13) = 79.5(3), Rh−C(1)−O(1) = 170.9(12).

The structures of **2a**,**c** were confirmed by X-ray crystallography. The structure of **2a**[8] is illustrated in Figure 1, and details of the structure of **2c** are provided as Supporting Information. The principal geometrical features of these five-membered metallacycles are very similar to those found in related Pd(II) systems.[7] The Rh−acetyl moiety adds to the exo face of the alkene double bond (and in the case of dicyclopentadiene, selectively at the nbd-like double bond). These observations represent the first well-characterized products of alkene insertion into a Rh−acyl bond. As well as being required for CO/alkene copolymerization, this process has been suggested as a possible step in catalytic or stoichiometric hydroacylation.[9,10] To our knowledge, the only other non-palladium system where analogous insertions have been observed is [RMn(CO)$_5$], for which high pressures were required.[11] Reactions of **1** with simple alkenes such as ethylene and 1-hexene were attempted but have so far not yielded isolable products.[12]

Kinetic studies have been conducted in order to probe the mechanistic details of the reactions of **1** with alkenes and with phosphines. The reactions with phosphines gave the expected products [Cp*Rh(CO)L(COMe)]$^+$ (L = PPh$_3$ (**3d**), PPh$_2$Me (**3e**), PPhMe$_2$ (**3f**); Scheme 4) resulting from methyl migration onto CO and coordination of phosphine. Complexes **3d**−**f** were fully characterized (as their BF$_4^-$ salts), including X-ray crystal structures, which will be reported elsewhere. Since typical reaction time scales were on the order of seconds, stopped-flow IR spectroscopy was employed for reaction monitoring. Pseudo-first-order conditions were employed, with the reactant ligand (alkene or phosphine) in at least a 10-fold excess over [**1**]. In each experiment, clean exponential decay of the reactant ν(CO) bands was observed, indicating a first-order dependence on **1**. Plots of k_{obs} vs [L] displayed saturation behavior, rising toward a limiting rate at high [L]. This is consistent with the mechanism shown in Scheme 4, with a rate-limiting, reversible methyl migration step (k_1).

Scheme 4. Mechanism of Reactions of 1 with Alkenes and Phosphines[a]



[a] L = nbd (**a**), nbe (**b**), dicyclopentadiene (**c**), PPh$_3$ (**d**), PPh$_2$Me (**e**), PPhMe$_2$ (**f**).

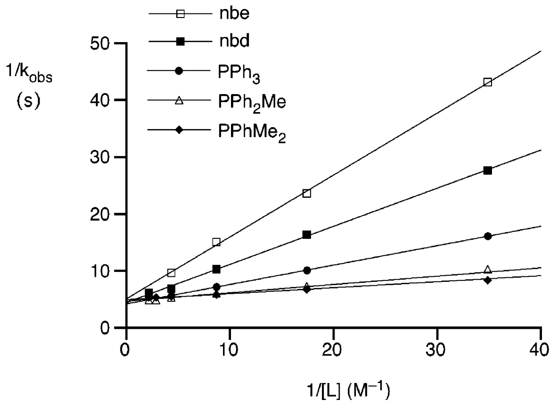


Figure 2. Plots of 1/k_{obs} vs 1/[L] for reactions of **1** (CH$_2$Cl$_2$, 25 °C).

For such a mechanism, a plot of 1/k_{obs} vs 1/[L] should be linear with *y* intercept 1/k_1 and slope k_{-1}/k_1k_2. The reciprocal plots shown in Figure 2 demonstrate clearly that the linear relationship holds with the same *y* intercept for each ligand, L. Thus, k_1 is independent of the nature of L for both phosphines and alkenes. An Eyring plot of variable-temperature data gave activation parameters $\Delta H^{\ddagger} = 72 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -16 \pm 6$ J mol^{-1} K^{-1} for methyl migration. The activation barrier is therefore much lower than for methyl migration in the isoelectronic group 8 analogue [CpRu(CO)$_2$Me], for which reaction with PPh$_3$ occurred at 137 °C with a rate constant of ca. 10^{-5} s^{-1}, equating to $\Delta G^{\ddagger} = 141$ kJ mol^{-1}.[13] This can be explained by the decreased back-bonding in the cationic complex **1**, resulting in more electrophilic CO ligands.

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[8] Crystallographic data for for **2a**[BF$_4$]: C$_{20}$H$_{26}$BF$_4$O$_2$Rh, M_r = 488.13, orthorhombic, a = 32.942(17) Å, b = 15.150(8) Å, c = 8.584(5) Å, *Pna*2$_1$ (C_{2v}^9 No. 33), Z = 8, T = 298(2) K, R1 = 0.0624 (on F^2) (wR2 = 0.1652 for all 9844 data).

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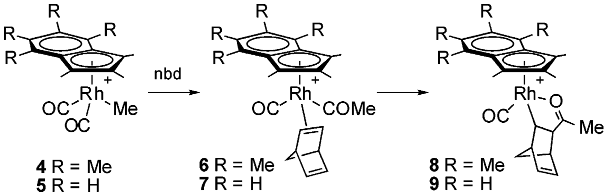
The slopes of the plots in Figure 2 give a measure of the ratio k_{-1}/k_2. Assuming that k_{-1} is independent of L, this gives an order of nucleophilicity toward the Rh intermediate $\mathbf{I_1}$ of nbe < nbd < PPh_3 < PPh_2Me < $PPhMe_2$, in broad agreement with expectation. The presumed intermediate species **3a**–**c** with an η^2-alkene coordinated cis to the acetyl ligand were not detected in these experiments, indicating that the subsequent alkene insertion step is fast (however, direct evidence for similar intermediates was obtained in a related system; see below).

For these Rh(III) systems to be active as CO/alkene copolymerization catalysts, chelate complexes of the type **2a**–**c** must undergo CO insertion. In tests on **2a**, however, we found no detectable reaction with CO at either atmospheric or elevated pressure (9 bar). Despite this, when **2a** was treated with 100 equiv of nbd in CH_2Cl_2, under 10 bar of CO at 40 °C, ca. 50% of the alkene was consumed after 5 days, as judged by the IR band of nbd at 1542 cm^{-1}. A strong broad product band at ca. 1720 cm^{-1} was observed in the region associated with organic keto functionalities.

One potential way to enhance the reactivity of chelate complexes such as **2a** is to replace Cp* by an indenyl ligand. Indenyl ligands are known to give dramatic accelerations (relative to their Cp analogues) of CO substitution,[14] and they also increase the rate of alkyl migration[15,16] and some catalytic reactions.[9,17] A number of Rh(I) complexes, $[(\eta^5\text{-}C_9Me_nH_{7-n})Rh(CO)_2]$, have been reported previously.[18] We found that oxidative addition of MeI to the η^5-C_9Me_7 (Ind*) and η^5-1,2,3-$Me_3C_9H_4$ (Ind′) complexes gave the expected iodo acetyl products. Iodide abstraction using $AgBF_4$ gave cations **4** and **5**, analogous to **1**. Kinetic measurements on the reaction of **4** with PPh_3 again showed saturation behavior, but the limiting rate constant at high [PPh_3] was found to be ca. 24 times faster (at 15 °C) than for **1**. This enhancement in the rate of methyl migration is very similar to that reported for $[IndMo(CO)_3Me]$ relative to $[CpMo(CO)_3Me]$.[15] Activation parameters for methyl migration in **4** are $\Delta H^\ddagger = 64 \pm 1$ kJ mol^{-1} and $\Delta S^\ddagger = -18 \pm 5$ J mol^{-1} K^{-1}, representing a lowering of $\Delta H^\ddagger$ relative to that for **1** of 8 kJ mol^{-1}.

Notably, in the reaction of **4** with nbd, evidence for an intermediate species was obtained. As the two terminal ν(CO) absorptions of **4** decayed, two new bands grew at 2061 and 1731 cm^{-1}. The intensity of these bands reached a maximum and then decayed, while absorptions of the final product **8** appeared at 2050 and 1625 cm^{-1}. The IR spectrum of the intermediate is consistent with a complex containing both terminal CO and acetyl ligands: i.e., prior to insertion of the alkene into the Rh-acetyl bond. We assign this species as the η^2-alkene complex **6**, which isomerizes to the insertion product **8** (Scheme 5). The buildup of detectable quantities of **6** can be explained if methyl migration is accelerated more than alkene insertion in the Ind* system. The half-life for alkene insertion in **6** is estimated as 0.6 s (15 °C), corresponding to $\Delta G^\ddagger$ = ca. 70 kJ mol^{-1}. This value is almost identical with that measured (at −46 °C) for ethene insertion in $[Pd(phen)(\eta^2\text{-}C_2H_4)(COMe)]^+$.[19] In preliminary kinetic experiments, the Ind′ complex **5** behaved similarly, with a rate constant for methyl migration ca. double that for **4**. An intermediate **7** (ν(CO) 2071, 1738 cm^{-1}) was again detected in the reaction of **5** with nbd.

Scheme 5. Reaction of Indenyl Complexes with nbd



Exposure of a CH_2Cl_2 solution of **8** to 1 atm of CO generated weak ν(CO) bands at 2129 (2118 sh) and 2102 (2089 sh) cm^{-1}, possibly indicative of a dicarbonyl product, $[Ind^*Rh(CO)_2(COC_7H_8COMe)]^+$. Treatment of **8** with 100 equiv of nbd in CH_2Cl_2, under 10 bar of CO, resulted in consumption of ca. 50% of the alkene after 3 days at 22 °C. After a further 2 days at 40 °C, all the alkene had reacted. On addition of a further 100 equiv of nbd, ca. 50% was consumed in 1 day at 40 °C, again leading to a strong broad ketone ν(CO) band at ca. 1720 cm^{-1}. Thus, catalytic activity appears to be significantly higher for the Ind* system relative to Cp*. Further experiments have indicated that the product of these catalytic reactions is polymeric (or oligomeric) in nature. Work is ongoing to determine the structural features of this polymer.

In summary, we have demonstrated that both of the key propagation steps for CO/alkene copolymerization are facile on Rh(III), leading to structurally characterized products. Intermediate Rh(η^2-alkene)(acetyl) complexes have been directly observed for indenyl sytems, and catalytic transformation of nbd and CO into polymeric products occurs under mild conditions.

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Supporting Information Available: Tables, text, and figures giving kinetic data, experimental details, spectroscopic and analytical data, and ORTEP plots and a CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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