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Synthesis, characterization and catalytic activity of a Wilkinson's type metal-organic–polyoxometalate hybrid compound

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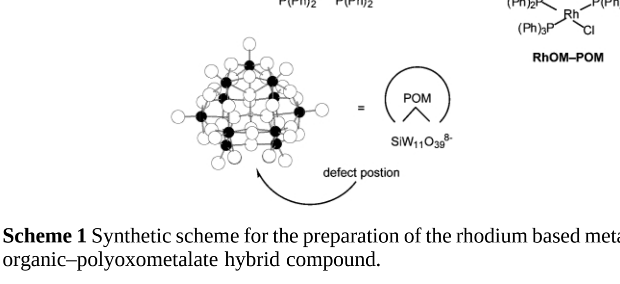
A metal-organic–polyoxometalate hybrid compound with two functional centers consisting of a rhodium(I)bis(diphenylphospine) unit connected through two alkylene bridging groups to a lacunary Keggin type polyoxometalate was synthesized and used as an effective, recyclable hydrogenation catalyst in monophasic and aqueous biphasic reaction modes.

Applications of polyoxometalates have become very important in diverse areas of research.[1] Especially, the use of polyoxometalates in catalysis has become extensive since the late 1970's.[2] Invariably, the catalytic use of polyoxometalates has been based on their inherent properties; high acidity in heteropoly acids, and favorable redox potentials and transition metal catalyic centers that make them attractive for applications in acid and oxidation catalysis. Another interesting area of activity in the chemistry of polyoxometalates has been their modification by metal-organic moieties.[3] Usually such compounds are based either on an electrostatic interaction of metal-organic cationic species with polyoxometalate anions or the attachment of an organic moiety to a metal center incorporated within the polyoxometalate cluster. Thus, for example, the possibility of combining noble metal based complexes and polyoxometalates for catalytic applications would also appear to be attractive and many noble metal complex–polyoxometalate hybrid compounds have been prepared.[3] Despite there being numerous metal-organic–polyoxometalate hybrid compounds, we know of only one application of such compounds in catalysis; the use of $[(PPh_3)_2Rh(CO)]_x[XW_{12}O_{40}]$ for a combined hydroformylation–oxidation reaction.[4]

In this paper, we present a new catalytically active noble metal metal-organic complex–polyoxometalate hybrid compound whereby a Wilkinson's type catalyst, Rh(I)Cl(Ph)$_3$, is covalently attached to a Keggin type polyoxometalate through an alkylene bridging spacer, Scheme 1.

Very recently, a Keggin type polyoxometalate was attached covalently *via* an alkylene spacer group to a metallosalen moiety; the polyoxometalate significantly modifies the electronic properties of the metallosalen unit.[5] The Rh(I) metal-organic–polyoxometalate compound, RhOM–POM, was used as an efficient hydrogenation catalyst in two ways. In the first case, a RhOM–POM complex was prepared that was soluble in organic solvents by using a lipophilic quaternary ammonium counter cation to the polyoxometalate unit. After completion of the reaction, the size and charge of the polyoxometalate moiety will potentially allow recovery of the catalyst by nanofiltration.[6] Alternatively, the catalyst may be precipitated and simply recovered by addition of ether. In the second case, a water soluble lithium salt of the RhOM–POM complex was prepared, leading to effective hydrogenation in an aqueous biphasic reaction mode that allows catalyst recovery by phase separation.



Scheme 1 Synthetic scheme for the preparation of the rhodium based metal-organic–polyoxometalate hybrid compound.

The preparation of the Rh(I) metal-organic–polyoxometalate hybrid compound was carried out according to the synthetic method outlined in Scheme 1, and is based on incorporation of a phosphine containing alkylsilane into the defect position of a lacunary polyoxometalate, $[SiW_{11}O_{39}]^{8-}$.[7,8] In this manner, the organosilane, $(OEt)_3SiCH_2CH_2PPh_2$, was reacted with the lacunary polyoxometalate leading to incorporation of the organosilane moiety into the defect position of the polyoxometalate, thereby yielding $K_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ in good yields.† The IR spectrum shows peaks at 1048 and 1123 cm^{-1} (Si–O bonds), 1001 cm^{-1} (W=O bonds) and 812, 931, 970 cm^{-1} (W–O–W bonds), attributable to the lacunary Keggin structure, that were unchanged by the modification with $SiCH_2CH_2PPh_2$ and absorption bands typical of a $SiCH_2CH_2PPh_2$ unit. In the ^{1}H NMR spectrum one observes peaks attributable to the CH_2CH_2 bridging unit and the aromatic rings. After metathetical exchange of the potassium cation with tetrabutylammonium the integration of the peaks observable for the tetrabutylammonium moiety can be used as internal reference for the incorporation of the $SiCH_2CH_2PPh_2$ units and clearly show the formation of $\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}^{4-}$.‡ The ^{29}Si NMR spectrum showed the necessary and expected peaks and intensities at -82.4 and -51.4 ppm for the polyoxometalate silicon heteroatom and two silicon atoms originating from the $SiCH_2CH_2PPh_2$ groups, respectively. The phosphorus atom is observed by ^{31}P NMR at -12.43 ppm. Importantly also, the ^{183}W NMR exhibited six peaks with relative intensities of 2 : 2 : 1 : 2 : 2 : 2, characteristic of the C_s symmetry of the polyoxometalate unit. The present $\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}^{4-}$ anion shows spectral properties very similar to the previously reported $\{SiW_{11}O_{39}[O(SiR)_2]\}^{4-}$ anions (R = $(CH_2)_3Cl$, $CH{=}CH_2$).[7]

The Wilkinson's type–polyoxometalate hybrid compound, $\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}^{4-}$, was obtained by reacting the phosphino functionalized polyoxometalate, $\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}^{4-}$, with a suitable rhodium compound, chlorobis(cyclooctene)rhodium(I), in the presence of one equivalent of triphenylphosphine.§ The compound is easily identifiable by the characteristic shift in the ^{31}P NMR spectrum due to complexation by Rh(I). Peaks at 17.33 and 36.46 ppm attributable to the triphenylphosphine and alkyldiphenylphospine ligands to Rh(I) were clearly observed.

As indicated above, the RhOM–POM hybrid complex was tested as an alkene hydrogenation catalyst in both (a) a single liquid organic phase reaction medium, 19 : 1 toluene : ethanol, using the $^8Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}$ (^{8}Q RhOM–POM; $^8Q = [(C_8H_{17})_3CH_3N^+]$) as catalyst and (b) an aqueous biphasic liquid–liquid reaction with a water soluble catalyst, $Li_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}$,

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Table 1 Hydrogenation of alkenes catalyzed by $\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}^{4-}$ using organic monophasic and aqueous biphasic reaction protocols

		Yield/mol%[a]	
Substrate	Product	Organic monophasic	Aqueous biphasic
1-Heptene	*n*-Heptane	99+	99+
1-Octene	*n*-Octane	99+	97
1-Decene	*n*-Decane	99+	98
trans-2-Octene	*n*-Octane	99+	99+
Styrene	Ethylbenzene	99+	99+
cis-Stilbene	Bibenzyl	99+	99+
Cyclohexene	Cyclohexane	99+	99

Reaction conditions: organic monophasic - 1 mmol alkene, 4 μmol $Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}$, 1 mL toluene–EtOH, 2 atm H_2, 2 h, 60 °C; aqueous biphasic - 1 mmol alkene, 0.25 mL of 1 mM $Li_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}$ in H_2O, 2 atm H_2, 2 h, 60 °C. The reaction mixtures were analyzed by GC and GC-MS.[a] Yields were measured by GC and is mol alkane/mol alkane + alkene + other products. Occasionally traces of isomerization products were observed.

(LiRhOM–POM) and a water immiscible alkene as substrate; no organic solvent was needed. From the results collected in Table 1, one can observe that the catalytic hydrogenation reactions proceeded smoothly to give alkanes from alkenes using both the monophasic and aqueous biphasic reaction protocols.

The catalytic efficiency of the QRhOM–POM, catalyst in the monophasic system was compared to that of the classic $(Ph_3P)_3Rh(I)Cl$ Wilkinson's catalyst using 1-octene as substrate (1 mmol 1-octene, 4 μmol QRhOM–POM, 1 mL toluene–EtOH, 2 atm H_2). The reaction rates were zero order with respect to both 1-octene and H_2. The rate constants under the given conditions 9.0×10^{-3} M min^{-1} and 5.8×10^{-3} M min^{-1} for QRhOM–POM and $(Ph_3P)_3Rh(I)Cl$, respectively. The Rh(I)metal-organic–polyoxometalate hybrid compound was a ~50% more effective catalyst on a molar basis, probably due to the presence of alkyl chains in the phosphine ligands, which provide improved stabilization of the intermediate Rh(III) species after oxidative addition of hydrogen. Catalyst recycle experiments showed that the water soluble LiRhOM–POM could be recovered by phase separation from the product (1-octene was hydrogenated under the conditions described in Table 1) and reused without loss of activity. Similarly, QRhOM–POM was recovered from the organic phase by addition of ether and reused without loss of activity.

These catalytic hydrogenation reactions represent the first example of the use of such metal-organic–polyoxometalate hybrid complexes as catalysts. Advantages that can be noted in the use of such hybrid complexes *versus* the classic Wilkinson's catalyst are the potential for dual applications, permitting catalyst separation by nanofiltration[9] or by phase separation.

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Notes and references

† $K_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ was synthesized by adding 6 mL $(EtO)_3SiCH_2CH_2PPh_2$ to a well stirred solution of $K_8SiW_{11}O_{39}$[10] (4 g, 1.34 mmol) in 100 mL of deionized water and 30 mL of acetonitrile under Ar. The pH was adjusted to pH = 1 by addition of 1 M HCl and vigorously stirred for 24 h. A white–yellow sticky precipitate of the undesired organosilicate oligomers, $(CH_2CH_2PPh_2SiO_{1.5})_n$, was removed by filtration and the acetonitrile was evaporated. Degassed isopropanol was added to the aqueous solution yielding as a white precipitate $K_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ (3.34 g, 75% yield). The dried powder was stored in a desiccator. IR (cm^{-1}): 507, 535, 690, 710, 812, 931, 970, 1001, 1048, 1123, 1179, 1278, 1405, 1440, 1485, 1588, 1619, 2907, 2957, 2996, 3059, 3083. ^{1}H-NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.52 (m, 4H, $SiCH_2$), δ = 2.05 (m, 4H, PCH_2), δ = 7.2–7.5 (m, 20H, Ar). {^{1}H}-decoupled ^{29}Si-NMR (79.495 MHz, [D$_6$]DMSO, 25 °C): $\delta = -82.4$ (1Si for the polyoxometalate heteroatom), $\delta = -51.4$ (2Si for the alkylsilyl groups). ^{31}P-NMR (101.271 MHz, [D$_6$]DMSO, 25 °C): $\delta = -12.43$ (bs). ^{183}W-NMR (16.671 MHz, [D$_6$]DMSO, 25 °C): $\delta = -245.83$ (s, 2W), $\delta = -170.10$ (s, 2W), $\delta = -122.68$ (d, 2W), $\delta = -110.11$ (s, 1W), $\delta = -105.81$ (s, 2W), $\delta = -104.79$ (s, 2W).

‡ $^4Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ was prepared by suspending $K_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ (33 mg, 10 μmol) in a few mL of degassed water; tetrabutylammonium chloride (11.6 mg, 44 μmol) dissolved in dichloromethane was added and the mixture was vigorously stirred under argon for three hours. The organic phase was separated and evaporated to dryness, leaving $^4Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ ^4Q = $[(C_4H_9)_4N^+]$ as a white powder. ^{1}H-NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 0.52 (m, 4H, $SiCH_2$), δ = 0.92 (t, 48H, $^+N(CH_2)_3CH_3$), δ = 1.31 (m, 32H, $^+N(CH_2)_2CH_2CH_3$), δ = 1.53 (m, 32H, $^+NCH_2CH_2CH_2CH_3$), δ = 2.05 (m, 4H, PCH_2), δ = 3.16 (t, 32H, $^+NCH_2CH_2CH_2CH_3$), δ = 7.2–7.5 (m, 20H, Ar).

§ $^8Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}$ was synthesized under argon by dissolving $^8Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$ (preparation the same as described above for $^4Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2]\}$) (47 mg) in toluene (2 mL) and adding chlorobis(cyclooctene)rhodium(I)[11] (0.5 μmol, 4 mM in toluene) followed by addition of triphenylphosphine (1 μmol) dissolved in toluene (0.5 mL). After few minutes ethanol (2 mL) was added to prevent dimerization at the Rh(I) center. $^8Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)2PPh_3Rh(I)Cl]\}$ was isolated after evaporation of the solvents. ^{31}P-NMR (101.271 MHz, [D8]toluene + 5% EtOH, 25 °C): δ = 17.33 (s, Ph_3PRh, 1P), δ = 36.46 (bs, CH_2Ph_2PRh, 2P). The lithium salt of $\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}^{4-}$ was used without isolation and was prepared by suspending the desired amount of $^4Q_4\{SiW_{11}O_{39}[O(SiCH_2CH_2PPh_2)_2PPh_3Rh(I)Cl]\}$ in deionized water followed by addition of five equivalents of LiCl. After vigorous mixing for two hours the suspension was filtered and the filtrate obtained was used directly for catalytic hydrogenation.

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