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Towards thermally robust homogeneous catalysts: Re, Ir and W complexes of the highly thermally stable ligand, tri-2-pyridylamine

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Abstract

The ligand tri-2-pyridylamine (tripyam (1)), which was expected to be highly resistant to thermal degradation, forms a variety of stable complexes with rhenium, tungsten and iridium. Reaction of 1 with ReCl₃(PPh₃) (benzil), WCl₄(PPh₃)₂ and (NH₄)₂IrCl₆ yields the chloride complexes ReCl₃(tripyam) (2), WCl₄(tripyam) (3) and IrCl₃(tripyam) (4), respectively. In addition, the first tripyam supported hydride, [IrH₂(PPh₃)₂(η^2 -tripyam)]BF₄ (5), was synthesized by reaction of 1 with the dihydride [IrH₂(PPh₃)₂(acetone)₂]BF₄. The principal characteristic of 2, 4 and 5 is their very high thermal stability: they survive thermolysis at temperatures up to 270 °C. Finally, the high oxidation state complexes [ReO₃(tripyam)]ReO₄ (6) and [ReO(OCH₂CH₂O)(PPh₃)(tripyam)]Cl (7) were also synthesized.

Keywords: Rhenium complexes; Iridium complexes; Tungsten complexes; Polydentate nitrogen ligand complexes

1. Introduction

A troublesome weakness of homogeneous versus heterogeneous catalysts is their much greater tendency to thermal deactivation, which often occurs by ligand degradation. Catalytic alkane dehydrogenation is a rigorous test of the stability of ligands, because even the most robust homogeneous catalysts available are still prone to degradation. The degradation pathway is known for catalysts such as $\operatorname{ReH}_{7}(\operatorname{PPh}_{3})_{2}[1]$ or $[IrH_2(OCOCF_3)(PR_3)_2]BF_4$ [2] in which the phosphine ligands undergo P-C bond cleavage [3]; orthometalation can also occur. Clearly, these problems might be avoided if a more robust, thermally stable ligand set were available. An important challenge in transition metal chemistry is the development of degradation resistant ligands that promote homogeneous catalysis. In earlier attempts to solve this problem, we looked at potentially more stable chelating phosphines [4] and also at non-phosphine ligands having structures that were designed to prevent or slow the known deactivation pathways [5]. These still proved to be unsuitable: the chelating phosphines were still found to degrade, and the nonphosphine ligands either degraded or simply failed to promote catalysis.

1.1. Choice of ligand for this work

We have continued our search for a degradation resistant ligand able to stabilize a wide range of organometallic compounds. The increasing interest in nitrogen donor ligands in homogeneous catalysis has prompted us to investigate this class of ligands. In particular, in this paper, we look at the tridentate nitrogen donor ligand, tri-2-pyridylamine (tripyam) (1) [6].



This system is particularly attractive because all the C-H bonds are held away from the metal and the amine nitrogen lone pair is not basic enough to favor tetradentate binding. In addition, the system is sufficiently sterically bulky to hinder binuclear deactivation pathways.

2. Results and discussion

Our first goal has been the development of the coordination chemistry of 1, with particular emphasis on catalytically active second and third row metals. Complexes of 1 have

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been previously studied, mainly of first row, rather than second and third row metals [7]. Unlike many standard ligands, 1 is expected to be very stable to oxidation, potentially allowing the synthesis of high oxidation state complexes and their use in catalytic oxidation. In this paper we report our results with rhenium, iridium and tungsten.

2.1. Preparation of complexes

2.1.1. Synthesis of ligand and of chloride precursor complexes

Tripyam was prepared by a modification of the method of Ref. [6] (see Section 4). Prior deactivation of the support with NEt₃ is necessary for efficient chromatographic separation.

The metal chloride complexes $\text{ReCl}_3(\text{tripyam})$ (2), WCl₄(tripyam) (3) ¹ and IrCl₃(tripyam) (4) were synthesized as shown in Eqs. (1), (2) and (3), as potential starting materials for the synthesis of catalyst precursors such as polyhydrides or silyl hydrides.



Reaction of Wilkinson's complex $\text{ReCl}_3(\text{benzil})(\text{PPh}_3)$ with tripyam overnight in refluxing benzene afforded a powdery chocolate brown compound, **2**, the identity of which was confirmed by ¹H NMR studies and from the FAB mass spectrum (m/e 539). Like many d⁴ species, this Re^{III} complex, $\text{ReCl}_3(\text{tripyam})$, displays a paramagnetic shift in its proton NMR spectrum. Resonances for tripyam are observed at 17.6 (dd, 3H), 16.8 (d, 3H), -4.79 (dd, 3H) and -18.8 (d, 3H) ppm, shifted from 8.21 (d, 3H), 7.64 (dd, 3H), 7.01 (dd, 3H) and 7.0 (d, 3H) ppm in free tripyam. The powdery tan complex $WCl_4(tripyam)$ (3) can be synthesized from $WCl_4(PPh_3)_2 \cdot CH_2Cl_2$ and tripyam in refluxing toluene. It is notable that tripyam displaces both of the PPh₃ groups. No ¹H NMR spectrum could be obtained for this paramagnetic d⁴ W^{IV} system, but elemental analyses and the IR spectrum, with typical tripyam bands at 1594, 1526, 1142, 1089, 1025 and 960 cm⁻¹, confirmed its identity. The hapticity of the tripyam ligand cannot be confirmed, however, as tripyam is known to form both bidentate and tridentate complexes, and crystals suitable for crystallography were not obtained.

The synthesis of IrCl₃(tripyam) (4) is based on that of McWhinnie and Kulasingam [7f] but modified to allow use of the more readily available $(NH_4)_2IrCl_6$ instead of IrCl₃. The addition of KI facilitates the normally slow reduction of IrCl₆²⁻ to IrCl₆³⁻ [8], thus enabling us to obtain 4 upon reaction with tripyam in refluxing water for 48 h. The ¹H NMR spectrum of 4 is characteristic for a complex with $C_{3\nu}$ symmetry, the tripyam protons being shifted downfield from 8.30 (dd, 3H), 7.72 (d, 3H), 7.1 (dd, 3H) and 7.0 (d, 3H) ppm (in the same solvent) to 8.95 (d, 3H), 8.25 (dd, 3H), 8.15 (dd, 3H) and 7.7 (d, 3H) ppm upon coordination, suggesting η^3 -coordination. Elemental analysis suggested the presence of 2 mol of crystallization of water, as also found by McWhinnie and Kulasingam, but the complex could not be dehydrated without decomposition.

2.2. Synthesis of [IrH₂(PPh₃)₂(tripyam)]BF₄

The first tripyam hydride has been synthesized by reaction of $[IrH_2(PPh_3)_2(acetone)_2]BF_4$ with tripyam, which produced a light yellow powdery dihydride $[IrH_2(PPh_3)_2(\eta^2$ tripyam)]BF_4 (5), where tripyam is bidentate.

$$[IrH_2(PPh_3)_2(acetone)_2]BF_4 + tripyam \longrightarrow H_{H_1} N_N N_N N_N M_N (4)$$

The triplet Ir-H resonance is shifted from -27.8 ppm in the starting material to -20.8 ppm (t, ${}^{2}J(\text{HP}) = 20$ Hz) in the tripyam hydride, 5. Additionally, the selectively proton-decoupled ${}^{31}\text{P}$ NMR spectrum shows a triplet at $\delta 20.7$ (${}^{2}J(\text{HP}) = 20$ Hz) indicating the presence of two hydride ligands. The characteristic resonance pattern for bidentate tripyam can be seen in the ¹H NMR with the unbound pyridyl group appearing at $\delta 8.02$ (d, 1H), 6.90 (dd, 1H), 6.77 (dd, 1H) and 5.13 (d, 1H), and the two bound pyridyl groups at $\delta 7.80$ (d, 2H), 7.45 (dd, 2H), 7.36 (d, 2H) and 6.15 (dd, 2H).

2.3. Thermal stability of MCl_x(tripyam)

The importance of metal polyhydrides in catalytic alkane dehydrogenation prompted us to attempt the synthesis of

¹ This complex was also synthesized in a different fashion by Cote [7c] by reaction of SOCl₂ in CH_2Cl_2 and they suggest that the tripyam ligand is bidentate.

Re(tripyam)H₅, W(tripyam)H₆ or IrH₅(tripyam) but these were not obtained from 2-4 under a variety of conditions commonly used. We instead attempted alkane dehydrogenation reactions using cyclooctane and pentadecane as substrate and solvent directly with 2-5 as catalysts. Although none of these complexes were catalytically active, these experiments showed that some of them are exceptionally thermally stable. For example, in refluxing pentadecane at 270 °C, ReCl₃(tripyam) and IrCl₃(tripyam) are recovered completely unchanged after 24 h. In contrast, WCl₄(tripyam) decomposes readily even at 100 °C with liberation of free tripyam.

Hydrides are normally thermally unstable at elevated temperatures, so it was a surprise to find that $[IrH_2(PPh_3)_2(\eta^2$ tripyam)]BF₄ is completely unchanged even on prolonged heating at 270 °C. Remarkably, the compound fails to give any of such normally rapid reactions as cyclometalation, loss of PPh₃, P-C cleavage or loss of H₂, even though a *cis*-IrH₂ group is present.

2.4. Synthesis and reactivity of [ReO₃(tripyam)]ReO₄

We wondered if tripyam would be able to stabilize metal oxo complexes [9] in the hope that these might catalyze useful oxidation reactions. We found that a tripyam rhenium oxo complex, $[ReO_3(tripyam)]ReO_4$ (6), can be prepared using a method



similar to the one known to be successful for the preparation of TpReO₃ [10]. This structure was confirmed both by IR and ¹H NMR spectroscopy. The Re=O stretching frequencies in the IR spectrum are shown in Table 1 where they are compared with ν (Re=O) for other related complexes. The $C_{3\nu}$ symmetry of **6** was confirmed by the ¹H NMR spectrum, where the tripyam ligand protons in **6** were found to be shifted from the free ligand values to 8.73 (d, 3H), 8.02 (dd, 3H), 7.43 (dd, 3H) and 7.20 (d, 3H) ppm. Microanalytical data

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Selected $\nu(Re=O)$ frequencies in the IR spectrum

Complex	ν (Re=O) (cm ⁻¹)	Ref.
[(tacn)ReO ₃]Cl	955, 930	[11]
TpReO ₃	944, 924, 911, 894	[10]
Cp*ReO ₁	909, 878	[12]
[(tripyam)ReO ₁]ReO ₄	908, 891, 878	
MeReO ₃	1005, 953	[13]

were never completely satisfactory because the insolubility of the complex prevented complete purification.

We attempted alkene dihydroxylation with this oxo tripyam complex using two strained alkenes, norbornene and norbornadiene, but no glycolate complexes could be isolated or detected by ¹H NMR spectroscopy either under thermal or photochemical conditions. We showed that a glycolate complex, 7, of the type that would result from alkene dihydroxylation, and similar to Wieghardt's [ReO-(OCH₂CH₂O)(tacn)]Br, can indeed be synthesized independently from ethylene glycol, ReOCl₃(PPh₃)₂ and tripyam as shown in Eq. (6).



[ReO(OCH₂CH₂O)(PPh₃)(η^2 -tripyam)]Cl appeared to have indeed formed and has been characterized by ¹H NMR data. The ¹H NMR spectrum shows a downfield shift of the protons adjacent to the nitrogen atoms in the pyridyl ring of tripyam, which are observed as doublets at δ 9.15 (1H) and 9.05 (2H) and a shift of the methylene protons of the bound glycolate to δ 2.95 (2H) and 2.85 (2H). A ³¹P NMR resonance appears at δ 26.7. Neither prolonged reaction times nor heating yielded the tridentate complex [ReO(OCH₂CH₂O)(η^3 -tripyam)]Cl. The bidentate character of the tripyam ligand in 7 is confirmed by ¹H NMR and the presence of PPh₃ is confirmed by ³¹P NMR. Efforts to remove the remaining PPh₃ thermally only led to decomposition. Reaction of 7 with acids fails to yield the diol, and even upon prolonged heating under vacuum, the complex does not appear to convert to the trioxo complex as occurs for the tach derivative [$\text{ReO}_3(\text{tach})$]Cl as shown in Eq. (7).

$$\begin{bmatrix} 0\\ || \\ LRe \\ 0 \end{bmatrix}^{+} \xrightarrow{\Delta H} \begin{bmatrix} 0\\ || \\ LRe \\ 0 \end{bmatrix}^{+} (7)$$

3. Conclusions

We find that the tripyam ligand forms a variety of coordination compounds. Although none were found to be catalytically active for the dehydrogenation of alkanes or the dihydroxylation of alkenes, the majority of the tripyam complexes studied, particularly those of rhenium and iridium are remarkably thermally stable, so they are indeed highly degradation resistant. These findings suggest that if the appropriate catalytic system can be identified, the use of tripyam may indeed lead to catalysts of exceptional thermal stability.

4. Experimental

All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. ¹H NMR spectra were recorded on a Bruker WM-250 spectrometer with the residual solvent as reference. ³¹P NMR spectra were recorded on a GE Omega 300 spectrometer at ambient temperature unless otherwise indicated. All chemical shifts are given in ppm. $^{31}P{^{1}H}$ NMR were recorded with 85% H₃PO₄ as the reference. IR spectra were recorded on a Nicolet 5-SX FT spectrometer. Elemental analyses were performed by Atlantic Microlab. THF, ether and hexanes were distilled from sodium benzophenone ketyl and dichloromethane from CaH. Ethanol and methanol were dried over molecular sieves and were stored under argon. KReO₄ and (NH₄)₂IrCl₆ were obtained from Johnson-Matthey. ReOCl₃(PPh₃)₂ [14], $\operatorname{ReCl}_{3}(\operatorname{benzil})(\operatorname{PPh}_{3})$ [15], $\operatorname{WCl}_{4}(\operatorname{PPh}_{3})_{2} \cdot \operatorname{CH}_{2}\operatorname{Cl}_{2}$ [16] and $[IrH_2(PPh_3)_2(acetone)_2]BF_4$ [17] were synthesized according to literature procedures. Methyllithium, superhydride, red-Al, NaBH₄, LiAlH₄, EtMgBr, NaOCHO and Et₃SiH were all used as received from Aldrich Chemical Co.

4.1. Syntheses

4.1.1. Tri-2-pyridylamine (1)

Complex 1 was prepared by a modification of the method reported by Wibaut and LaBastide [6]. A 250 ml round bottom flask was charged with di-2-pyridylamine (34.24 g, 0.2 mol), 2-bromopyridine (57.2 ml, 0.6 mol), mesitylene (50 ml), sodium carbonate (20 g), copper powder (0.5 g) and a trace of potassium bromide. This solution was heated at 160 °C for 18 h. The solution was then cooled to room temperature and the excess copper powder and sodium carbonate was filtered off. The filtrate was then vacuum distilled to remove mesitylene and excess 2-bromopyridine, which were recovered. The remaining brown oil, containing unreacted di-2-pyridylamine and tri-2-pyridylamine, was cooled and redissolved in dichloromethane. This mixture was then purified using column chromatography on a SiO₂ column pretreated with NEt₃, on elution with a 5:1 mixture of ethyl acetate/heptanes. The di-2-pyridylamine eluted first and the tri-2-pyridylamine eluted second and was obtained as yellowish crystals, which were recrystallized from ethanol as pale yellow needles (24.8 g, 50% yield). ¹H NMR (400 MHz, acetone-d₆): δ 8.21 (d, J=4.8 Hz, 3H), 7.64 (dd, J = 7.3, 7.3 Hz, 3H, 7.01 (dd, J = 7.3, 4.8 Hz, 3H), 7.00 (d, J = 7.3 Hz, 3H; (250 MHz, dmso-d₆): $\delta 8.3$ (d, J = 4.5 Hz, 3H), 7.7 (dd, J = 8.3, 8.3 Hz, 3H), 7.1 (dd, J = 8.3, 4.5 Hz, 3H), 7.0 (d, J = 8.3 Hz, 3H). IR (Nujol): ν (tripyam) 1583, 1563, 1158, 1146, 1047, 993, 979, 777, 739 and 719 cm⁻¹.

4.1.2. Trichloro(tri-2-pyridylamine)rhenium(III) (ReCl₃(tripyam))(2)

To a solution of ReCl₃(benzil)(PPh₃) (0.20 g, 0.27 mmol) in dry degassed toluene (10 ml), was added a solution of tripyam (0.10 g, 1.41 mmol) in toluene (5 ml). The solution was then refluxed for 3 h during which time the bright purple color became chocolate brown. The solution was cooled, filtered and washed with ethanol and diethyl ether and dried under vacuum. A powdery, chocolate brown solid was obtained which could not be recrystallized because of decomposition and poor solubility (0.11 g, 77% yield). ¹H NMR (250 MHz, CD₂Cl₂): δ 17.6 (d, J = 8.0 Hz, 3H), 16.8 (dd, J = 8.0, 5.4 Hz, 3H), -4.79 (dd, J = 8.0, 8.0 Hz, 3H), -18.8 (d, J = 5.4 Hz, 3H). FAB-MS: m/e 539.

4.1.3. Tetrachloro(tripyam)tungsten (IV) (WCl₄(tripyam))(3)

To a solution of WCl₄(PPh₃)₂·CH₂Cl₂ (0.20 g, 0.21 mmol) in dry degassed toluene (10 ml) was added a solution of tripyam (0.054 g, 0.22 mmol) in toluene (5 ml). The solution was refluxed for 4 h during which time the bright yellow-orange color became light tan. The solution was filtered, washed with toluene, ethanol and diethyl ether and dried in vacuo to yield a powdery tan solid (0.09 g, 78% yield). IR (Nujol): ν (tripyam) 1595, 1142, 1089, 1025 and 960 cm⁻¹. Anal. Calc. for C₁₅H₁₂N₄Cl₄W·C₇H₈: C, 39.7; N, 8.41; H, 3.03. Found: C, 40.1; N, 8.45; H, 3.04%.

4.1.4. Trichloro(tripyam)iridium (III) (IrCl₃(tripyam)) (4)

To a solution of H₂O (10 ml) and $(NH_4)_2IrCl_6$ (0.10 g, 0.226 mmol) was added KI (0.226 mmol, 0.38 g). Tripyam (0.056 g, 0.226 mmol) was then added and the solution was refluxed for 48 h during which time the color changed from deep red-brown to light yellow with the formation of a precipitate. The solution was cooled to room temperature and filtered to yield a light yellow powdery solid. This was washed with Et₂O (10 ml) and dried in vacuo to afford a powdery yellow solid (0.48 g, 71% yield). ¹H NMR (250 MHz, dmso-d₆): δ 8.95 (d, J = 7.5, 4.7.5 Hz, 3H), 8.15 (dd, J = 7.5, 5.0 Hz, 3H), 7.7 (d, J = 7.5 Hz, 3H). *Anal.* Calc. for C₁₅H₁₂N₄Cl₃Ir · 2H₂O: C, 30.9; H, 2.70; N, 9.60. Found: C, 31.1; H, 2.27; N, 9.17%.

4.1.5. $[IrH_2(PPh_3)_2(\eta^2 - tripyam)]BF_4(5)$

A solution of $[IrH_2(PPh_3)_2(acetone)_2]BF_4$ (0.10 g, 0.11 mmol) and freshly distilled methylene chloride (10 ml) was degassed using the freeze-pump-thaw method (5 times). Tripyam (0.034 g, 0.14 mmol) was then added to the solution. This solution was then stirred at room temperature for 3 h after which time a pale yellow precipitate formed. This was filtered and recrystallized from CH₂Cl₂/hexanes to yield a powdery pale yellow solid (0.07 g, 76% yield). ¹H NMR (400 MHz, acetone-d₆): δ (tripyam) 8.02 (d, J=5.2 Hz, 1H), 7.80 (d, J=5.2 Hz, 2H), 7.45 (dd, J=7.3, 7.3 Hz, 2H), 7.36 (d, J=7.3, 5.2 Hz, 1H), 6.15 (dd, J=7.3, 5.2 Hz, 2H),

5.13 (d, J = 7.3 Hz, 1H); (PPh₃): 7.16, 7.01 (m, 30 H); (Ir-H): -20.8 (t, ${}^{2}J$ (HP) = 20 Hz, 2H). ${}^{31}P$ NMR (300 MHz, acetone-d₆): δ 20.7 (t, ${}^{2}J$ (HP) = 20 Hz). Anal. Calc. for C₅₁H₄₄N₄P₂F₄BIr · 2H₂O: C, 58.12; H, 4.20; N, 5.31. Found: C, 57.88.1; H, 4.27; N, 5.14%.

4.2. Alkane activation and thermal stability studies

4.2.1. Cyclooctane

In a typical experiment the complex (0.010 mmol), cyclooctane (11.15 mmol, 1.5 ml) and tert-butylethylene (0.78 mmol, 0.10 ml) were placed in a resealable triple-thickness 10 ml glass vessel equipped with a Teflon stopcock. This was degassed with five freeze-pump-thaw cycles. The vessel was then filled with argon and was heated for 24 h with magnetic stirring at 165 °C in a thermally equilibrated silicon oil bath. After cooling, an aliquot of the organic layer was removed and was analyzed by GC. The organometallic residue was redissolved in CD_2Cl_2 or acetone-d₆ and analyzed by ¹H NMR.

4.2.2. Pentadecane

In a typical experiment the complex (0.30 mmol) and pentadecane (2 ml) were added to a triple thickness 10 ml glass vessel equipped with a Teflon stopcock. This was degassed with five freeze-pump-thaw cycles. The vessel was then filled with argon and was heated for 24 h with magnetic stirring at 270 °C in a thermally equilibrated bath of Wood's metal. After cooling, an aliquot of the organic layer was removed and was analyzed for the presence of pentadecene by ¹H NMR (CDCl₃). The organometallic residue was redissolved in CD₂Cl₂ or acetone-d₆ and analyzed by ¹H NMR.

4.2.3. Trioxo(tripyam)rhenium(VII)perrhenate ([ReO₃(tripyam)]ReO₄)(6)

To a solution of Re₂O₇ (1.0 mmol, 0.484 g) in freshly distilled THF (10 ml) was added solid tripyam (1.0 mmol, 0.248 g). The solution was stirred at room temperature for 3.5 h. The cloudy light blue solution was then filtered to yield an insoluble light blue powdery solid. This was washed with Et₂O (10 ml) and was dried in vacuo (0.58 g, 79% yield). ¹H NMR (250 MHz, dmso-d₆): δ (tripyam) 8.73 (d, J = 5.2Hz, 3H), 8.02 (dd, J = 8.3, 8.3 Hz, 3H), 7.43 (dd, J = 8.3, 5.2 Hz, 3H), 7.20 (d, J = 8.3 Hz, 3H). IR: ν (Re=O): 908.0 (ReO₄ ⁻), 891.4, 878.5 (LReO₃). Anal. Calc. for C₁₅H₁₂O₇N₄Re₂: C, 24.7; H, 1.65; N, 7.64. Found: C, 25.3; H,1.95; N, 7.58%.

4.2.4. $[ReO(OCH_2CH_2O)(PPh_3)(tripyam)]Cl(7)$

To a solution of $\text{ReOCl}_3(\text{PPh}_3)_2$ (0.94 mmol, 0.79 g) in freshly distilled THF (10 ml) was added tripyam (2.01 mmol, 0.50 g) and freshly distilled ethylene glycol (1.4 mmol, 0.089 g, 0.08 ml). The solution was stirred for 2 h during which time the reaction changed from a green solution to a light purple solution. The solution was filtered and washed with THF (10 ml) and Et₂O (10 ml) to yield a light purple powdery solid. Due to the extreme insolubility of this complex, no further purification was possible. ¹H NMR (250 MHz, dmso-d₆): δ (tripyam): 9.15 (d, J = 4.6 Hz, 1H), 9.05 (d, J = 4.6 Hz, 2H); (tripyam, Ph): 8.4 -7.5 (m, 18 H); (tripyam): 7.25 (dd, J = 8.3, 4.6 Hz, 1H), 7.10 (d, J = 8.3 Hz, 1H), 7.0 (dd, J = 8.3, 4.6 Hz, 2H), 6.7 (d, J = 8.3 Hz, 2H); 2.95 (d, J = 6.3 Hz, OCH₂CH₂O), 2.85 (d, J = 6.3 Hz, OCH₂CH₂O). ³¹P NMR (dmso-d₆, 298 K): δ 26.7. IR (Nujol): (Re=O) 945 cm⁻¹. Anal. Calc. for C₃₅H₃₁O₃-N₄RePCl: C, 52.01; H, 3.86; N, 6.93. Found: C, 51.79; H, 3.95; N, 7.11%.

4.3. Attempted catalytic oxidation reactions of 6 with alkynes and strained alkenes

To a solution of 6 (0.0073 g, 0.009 mmol) in acetone (1 ml) was added phenylacetylene (0.55 ml) and 'BuOOH (0.09 ml) and the reaction was stirred at r.t. for 24 h. The organic products were analyzed by ¹H NMR spectroscopy. No oxidation products were found. Similar reactions were performed using norbornene and norbornadiene.

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