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Oxorhenium Complexes Bearing the Water-Soluble Tris(pyrazol-1-yl)methanesulfonate, 1,3,5-Triaza-7-phosphaadamantane, or Related Ligands, as Catalysts for Baeyer−Villiger Oxidation of Ketones

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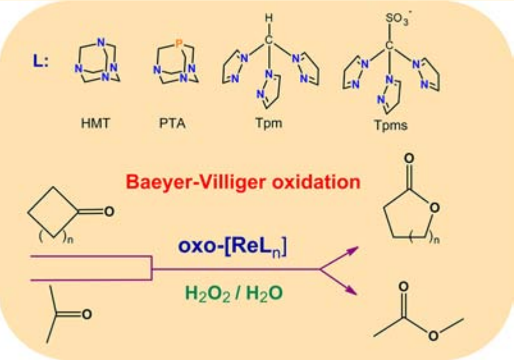
Supporting Information



ABSTRACT: New rhenium(VII or III) complexes $[ReO_3(PTA)_2][ReO_4]$ (**1**) (PTA = 1,3,5-triaza-7-phosphaadamantane), $[ReO_3(mPTA)][ReO_4]I$ (**2**) (mPTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane cation), $[ReO_3(HMT)_2][ReO_4]$ (**3**) (HMT = hexamethylenetetramine), $[ReO_3(\eta^2\text{-Tpm})(PTA)][ReO_4]$ (**4**) [Tpm = hydrotris(pyrazol-1-yl)-methane, $HC(pz)_3$, pz = pyrazolyl], $[ReO_3(Hpz)(HMT)][ReO_4]$ (**5**) (Hpz = pyrazole), [ReO(Tpms)(HMT)] (**6**) [Tpms = tris(pyrazol-1-yl)methanesulfonate, $O_3SC(pz)_3^-$] and $[ReCl_2\{N_2C(O)Ph\}(PTA)_3]$ (**7**) have been prepared from the Re(VII) oxide Re_2O_7 (**1**−**6**) or, in the case of **7**, by ligand exchange from the benzoyldiazenido complex $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$, and characterized by IR and NMR spectroscopies, elemental analysis and electrochemical properties. Theoretical calculations at the density functional theory (DFT) level of theory indicated that the coordination of PTA to both Re(III) and Re(VII) centers by the P atom is preferable compared to the coordination by the N atom. This is interpreted in terms of the Re−PTA bond energy and hard−soft acid−base theory. The oxo-rhenium complexes **1**−**6** act as selective catalysts for the Baeyer−Villiger oxidation of cyclic and linear ketones (e.g., 2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone, cyclobutanone, and 3,3-dimethyl-2-butanone or pinacolone) to the corresponding lactones or esters, in the presence of aqueous H_2O_2. The effects of a variety of factors are studied toward the optimization of the process.

1. INTRODUCTION

Recently, the coordination chemistry of the water-soluble cagelike aminophosphine 1,3,5-triaza-7-phosphaadamantane (PTA) has experienced rapid development, mainly justified by the search for new water-soluble transition-metal aminophosphine complexes particularly suited to serve as catalyst precursors in aqueous organometallic catalysis,[1,2] water-soluble antitumor agents,[1,3−5] or photoluminescent materials,[1,6,7a,b] and as the main organic linker in coordination polymers.[7c]

Among the transition-metal complexes bearing PTA or its derivatives, ruthenium (e.g., $[RuCl_2(PTA)_4]$ or $[RuCl_2(CO)(PTA)_3]$) and rhodium (e.g., $[RhI_4(mPTA)_2]I$, where mPTA = *N*-methyl-1,3,5-triaza-7-phosphaadamantane cation) complexes[8] have attracted considerable interest, because of their catalytic potential for a variety of processes under aqueous or biphasic conditions. On the other hand, the coordination chemistry of PTA to rhenium is also a matter of high current interest concerning the electrochemical behavior,[9] photophysical activity,[10] therapeutic and diagnostic applications as radiopharmaceuticals, of the obtained complexes.[11,12] An interesting feature revealed by certain PTA-Re complexes[13] is the ambivalent behavior concerning solubility in water and in organic solvents, which can be adjusted by the ligand protofilic properties. This has important implications for the separation and recycling of catalysts under biphasic conditions. Moreover, trioxorhenium complexes have been regarded as efficient catalysts for the oxidation of a variety of organic substrates[14−21] and very useful starting reagents in coordination chemistry.[21−26]

As an extension of the above synthetic and catalytic directions, the present work aims at the easy preparation of new water-soluble Re complexes bearing PTA-type ligands (Figure 1) and probing their catalytic potential in mild oxidative conversions of ketones. Hence, within the search for a suitable starting material for the synthesis of new water-

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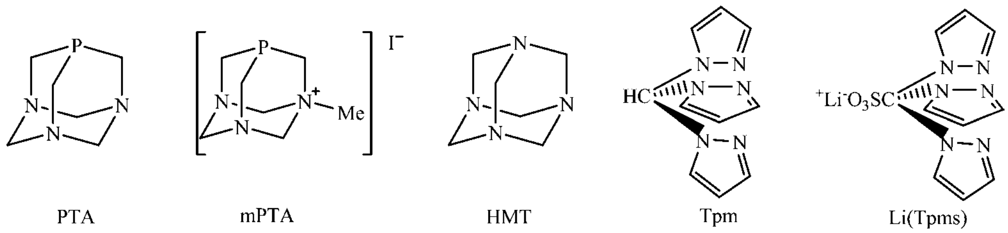


Figure 1. 1,3,5-Triaza-7-phosphaadamantane (PTA), its *N*-methylated derivative (mPTA) salt, hexamethylenetetramine (HMT), hydrotris(pyrazol-1-yl)methane (Tpm), and lithium tris(pyrazol-1-yl)methanesulfonate Li(Tpms).

soluble Re complexes, we have chosen Re_2O_7, which is a relatively inexpensive, accessible, and highly reactive material; in the presence of the water-soluble cagelike phosphanes PTA or [Me-PTA]I (*N*-methyl-1,3,5-triaza-7-phosphaadamantane iodide), or of HMT (hexamethylenetetramine), at room temperature, this material led to $[ReO_3(PTA)_2][ReO_4]$ (**1**), $[ReO_3(mPTA)][ReO_4]I$ (**2**) and $[ReO_3(HMT)_2][ReO_4]$ (**3**), respectively (see reactions a–c in Scheme 1).

Moreover, the preparation, by some of us,[27] of the first water-soluble transition metal complex bearing simultaneously PTA and $Tpms^-$ (tris(pyrazol-1-yl)methanesulfonate), [Rh(Tpms)(CO)(PTA), in high yield, by a single-pot reaction of $[\{Rh(CO)_2(\mu\text{-Cl})\}_2]$, PTA and Li(Tpms), prompted us, in the current work and in pursuit to our interest on the coordination chemistry of C-scorpionates,[28] to react Re_2O_7 with PTA and Tpm, or HMT and Li(Tpms) (Figure 1), at room temperature. This has led to the new water-soluble and stable oxo-rhenium complexes $[ReO_3(\eta^2\text{-Tpm})(PTA)][ReO_4]$ (**4**), $[ReO_3(Hpz)(HMT)][ReO_4]$ (**5**) and [ReO(Tpms)(HMT)] (**6**) (see reactions d–f in Scheme 1).

The study we now report also aims to achieve water-soluble Re compounds prepared, from hydro- insoluble ones, by ligand exchange reactions, as known[29] for the nitridorhenium(V) $[ReNCl_2\ (PTA)_3]$ and *trans*-dioxorhenium(V) $[ReO_2Cl(PTA)_3]$ complexes obtained from $[ReNCl_2(PPh_3)_2]$ or $[ReOCl_2X(PPh_3)_2$ (X = Cl^-, OMe^-, OEt^-), respectively. The replacement of the PPh_3 and Hpz ligands at our $[ReCl_2\{N_2C(O)Ph\}(Hpz)_2(PPh_3)_2]$[28b] was successful and led to the formation of the new benzoyldiazenido PTA complex $[ReCl_2\{N_2C(O)Ph\}(PTA)_3]$ (**7**) (see Scheme 2).

Transition-metal-catalyzed Baeyer–Villiger (BV) oxidations, viz, the transformation of cyclic and acyclic ketones into lactones and esters, has become an important research topic recently,[30−48] because of the wide applications of the products in fine chemical industry. For economic and environmental reasons, a growing amount of attention has been paid to the replacement of the classical use of organic peroxyacids by more atom-efficient and environmentally friendly oxidants, such as molecular oxygen[49−51] or hydrogen peroxide.[31,38−40,44,52,53] Moreover, the recognized application of the versatile complex $[(Me)ReO_3]$ (MTO) in oxidation catalysis, including the BV oxidation of ketones,[40,53] clearly demonstrates the ability of rhenium centers to form highly active catalysts for the oxidation reactions of olefins and other unsaturated substrates. It has been found that rhenium complexes bearing oxo- or *N*-ligands (such as benzoyl-diazenido or benzoyl-hydrazido, C-scorpionates, or pyrazoles) act as selective catalysts (or catalyst precursors), in homogeneous systems, for the oxidation and carboxylation of inert alkanes, under mild or moderate conditions[54−56] and are also active in BV oxidation reactions.[57]

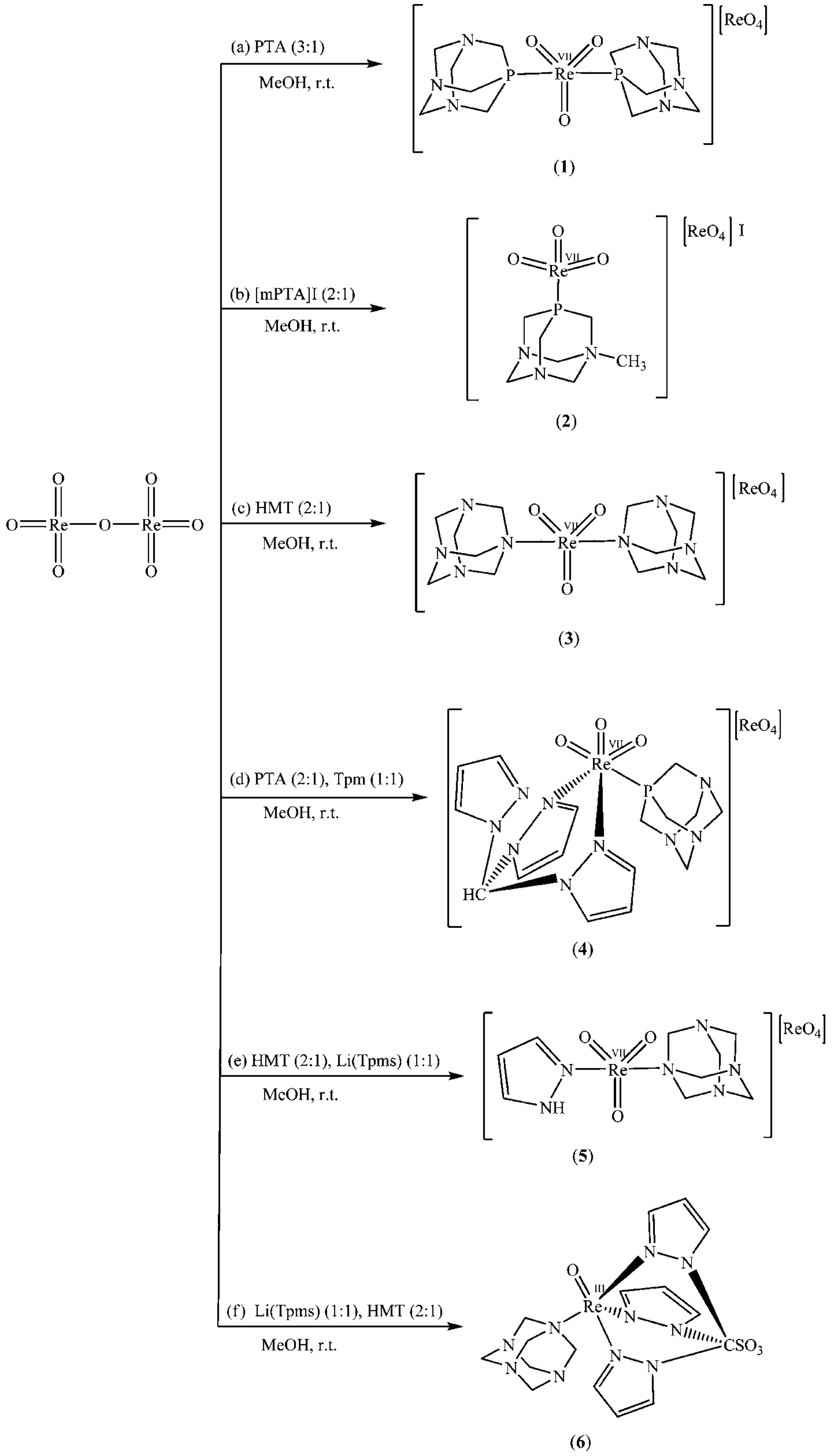
Aiming to contribute toward the development of the still little-explored application of Re compounds as catalyst and/or catalyst precursor for the oxidation of ketones to the respective esters or lactones, under relatively mild conditions and with an environmentally friendly oxidant (H_2O_2), we now report the BV oxidation, by aqueous H_2O_2 in 1,2-dichloroethane, of cyclic and linear ketones catalyzed by **1–6** (see Scheme 3, presented later in this paper).

2. EXPERIMENTAL SECTION

Materials and Instrumentation. The synthetic work was carried out under an oxygen-free dinitrogen atmosphere, using standard Schlenk techniques. K[ReO$_4$] (Aldrich), Re_2O_7 (Aldrich), hexamethylenetetramine (HMT), pyrazole (Aldrich), 2-methylcyclohexanone (Aldrich), 2-methylcyclopentanone (Aldrich), cyclopentanone (Aldrich), cyclohexanone (Aldrich), cyclobutanone (Aldrich), 3,3-dimethyl-2-butanone (pinacolone) (Aldrich), *δ*-hexalactone (Aldrich), *ϵ*-caprolactone (Aldrich), *δ*-valerolactone (Aldrich), *β*-butyrolactone (Aldrich), *tert*-butylacetate (Aldrich), 1,2-dichloroethane (Aldrich), dichloromethane (Fluka), toluene (Fluka), methanol (Fluka), hydrogen peroxide (30%) (Fluka), cycloheptanone (Aldrich), diethyl ether (Riedel-de-Haën), and dinitrogen gas (Air Liquid Portugal) were used as received from the suppliers. The solvents were dried over appropriate drying agents and degassed by standard methods.

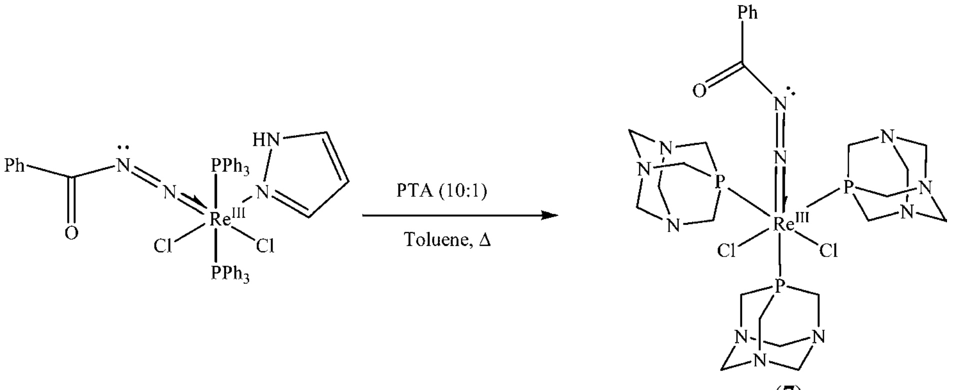
The C-scorpionates hydrotris(pyrazol-1-yl)methane (Tpm)[58] and lithium tris(pyrazol-1-yl)methane sulfonate (LiTpms),[59] the aminophosphines 1,3,5-triaza-7-phosphaadamantane (PTA) and *N*-methyl-1,3,5-triaza-7-phosphaadamantane iodide ([mPTA]I),[60] as well as $[ReCl_2(\eta^2\text{-}N,O\text{-}N_2C(O)Ph)(PPh_3)_2]$[61] and $[ReCl_2(N_2C(O)Ph)(Hpz)(PPh_3)_2]$,[28b] were prepared in accordance with published procedures. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico, Lisbon. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD Model FTS 3000MX instrument using KBr pellets. Far-infrared spectra (400–200 cm^{-1}) were recorded on a Bruker Vertex instrument using polyethylene pellets. ^1H, ^{13}C, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and COSY NMR spectra were measured on Bruker 300 and 400 UltraShield spectrometers at room and low temperatures. ^1H and ^{13}C chemical shifts (δ) are expressed in ppm, relative to $Si(Me)_4$, whereas $\delta(^{31}P)$ chemical shifts are relative to 85% H_3PO_4. Coupling constants are given in units of Hz (abbreviations: s, singlet; d, doublet; t, triplet; m, complex multiplet; vt, virtual triplet; br, broad). ^1H DOSY NMR spectrum was obtained on a 500 MHz Bruker Avance III spectrometer from a DMSO-d_6 solution of the complex at 23 °C using a 5-mm probe. In the PFG NMR experiments, a bipolar stimulated echo pulse sequence was used. The duration of the pulse gradients (1.2 ms) and the diffusion time (60 ms) were adjusted in order to obtain full attenuation of signals at 95% of maximum gradient strength. The gradient strength was incremented from 2% to 95% in a linear ramp with 16 steps. A delay of 10 s between echoes was used. The numbering of the pyrazolyl ring is as follows: Re–N(1)N(2)C(3)-HC(4)HC(5)H. The C, H, N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer (PC) through a GPIB interface. Cyclic voltammetry (CV) studies were

Scheme 1. Syntheses of Compounds 1−6



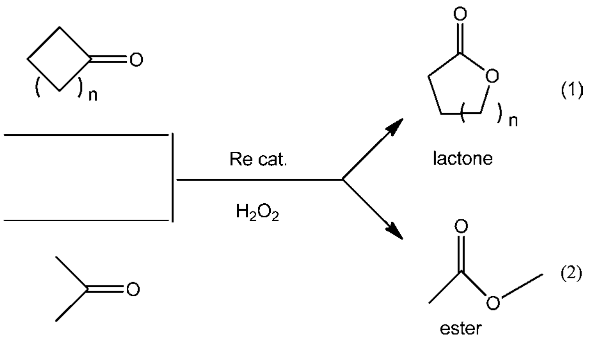
undertaken in 0.2 M [^{n}Bu$_4$N][BF$_4$]/DMSO, at a platinum-disk working electrode (d = 0.5 mm) and at room temperature. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. A Pt wire was employed as the counter-electrode for the CV cell. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring no significant potential drift occurred along the electrolyses. The solutions were saturated with N_2 by

Scheme 2. Synthesis of Complex $[ReCl_2\{N_2C(O)Ph\}(PTA)_3]$ (7)



(7)

Scheme 3. Baeyer–Villiger (BV) Oxidation of Cyclic (1) and Acyclic (2) Ketones



bubbling this gas before each run, and the redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and their values are quoted relative to the SCE, using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.44 V vs SCE).[62] Gas chromatography (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length = 30 m; internal diameter = 0.32 mm). The temperature of injection was 240 °C. The initial temperature was maintained at 80 °C for 1 min, then increased at a rate of 10 °C/min up to 140 °C (in the case of pinacolone oxidation) or 180 °C, and held at this temperature for 1 min. Helium was used as the carrier gas.

Syntheses and Characterization of the Complexes. *$[ReO_3(PTA)_2][ReO_4]$ (1).* To a stirred solution of Re_2O_7 (100.0 mg, 0.206 mmol) in MeOH (10 mL) a 3:1 molar amount of PTA (97.3 mg, 0.619 mmol) in MeOH was added, yielding a yellow solid, which was isolated by filtration and washed with MeOH (10 mL). **1** is soluble in H_2O ($S_{25°C} \approx 16.7$ mg mL^{-1}). Yield = 58%, based on Re_2O_7. **1**, $C_{13}H_{28}N_6O_8P_2Re_2$ (830.8): Calcd. C 18.8, N 10.1, H 3.4; Found C 18.2, N 10.1, H 3.6. IR (KBr): 2919 cm^{-1} [asym C–H, (CH_2) (PTA)], 2874 [sym C–H, (CH_2) (PTA)], 1416 [asym P–CH_2, (PTA)], 1310 [sym P–CH_2, (PTA)], 1288 [N–CH_2, (PTA)], 1242 [N–C–N, (PTA)], 1014 [N–C–N, (PTA)], 911 [Re=O]. ^1H NMR (400 MHz, D_2O): δ 4.69 and 4.53 ($J(H^AH^B)$ = 12 Hz, 12H, NCH^AH^BN (PTA)) 4.20 (s, 12H, PCH_2N (PTA)), 3.15 (s, 3H, MeOH). $^{13}C\{^1H\}$NMR (100 MHz, D_2O): 71.2 (s, NCH_2N), 46.90 (d, $^1J(CP)$ = 20.5 Hz, PCH_2N). $^{31}P\{^1H\}$NMR (162 MHz, D_2O): −70.1 (s).

$[ReO_3(mPTA)][ReO_4]I$ (2). A 2:1 molar amount of [mPTA]I (123.2 mg, 0.412 mmol) in MeOH was added to a stirred solution of Re_2O_7 (100.0 mg, 0.206 mmol) in MeOH (30 mL), yielding a brown solid, which was isolated by filtration and washed with MeOH (10 mL). **2** is soluble in H_2O ($S_{25°C} \approx 4.2$ mg mL^{-1}). Yield = 69%, based on Re_2O_7. **2**, $C_8H_{19}IN_3O_8PRe_2$ (815.5): Calcd. C 11.8; H 2.3; N 5.2; Found C 11.7, H 2.3, N 6.0. IR (KBr): 1452 [asym P–CH_2, (mPTA)], 1250 [C–N, (mPTA)] cm^{-1}, 910 (Re=O). ^1H NMR (400 MHz, D_2O): δ 5.00 and 4.85 ($J(H^AH^B)$ = 12 Hz, 4H, $NCH^AH^BN^+$), 4.80 and 4.27 ($J(H^AH^B)$ = 13 Hz, 2H, NCH^AH^BN), 4.52 (s, 2H, PCH_2N^+), 4.17 and 3.95 ($J(H^AH^B)$ = 15.0 Hz, 4H, PCH^AH^BN), 3.18 (s, 3H, MeOH), 2.67 (s, 3H, N^+CH_3). $^{13}C\{^1H\}$NMR (100 MHz, D_2O): 82.5 (s, NCH_2N^+), 70.3 (s, NCH_2N), 57.3 (s, PCH_2N^+), 51.3 (s, CH_3), 48.7 (s, PCH_2N). $^{31}P\{^1H\}$NMR (162 MHz, D_2O): −69.1 (s).

$[ReO_3(HMT)_2][ReO_4]$ (3). A 2:1 molar amount of HMT (57.8 mg, 0.412 mmol) in MeOH was added to a stirred solution of Re_2O_7 (100.0 mg, 0.206 mmol) in MeOH (10 mL), yielding a brown solid, which was isolated by filtration and washed with MeOH (10 mL). Yield = 46%, based on Re_2O_7. **3** is soluble in H_2O ($S_{25°C} \approx 25$ mg mL^{-1}). $C_{13}H_{28}N_8O_8Re_2$ (796.8): Calcd. C 19.6, N 14.1, H 3.5; Found C 19.2, N 14.6, H 3.5. IR (KBr): 1265 [C–N, (HMT)] cm^{-1}, 910 (Re=O). ^1H NMR (400 MHz, D_2O): δ 4.61 (s, br, 6H, NCH_2N (HMT)), 4.40 (s, br, 6H, $N^{coord}CH_2N$ (HMT)), 3.14 (s, 3H, MeOH). $^{13}C\{^1H\}$NMR (100 MHz, D_2O): 71.2 (s, NCH_2N, HMT). ^1H DOSY NMR (500 MHz, DMSO-d_6): log D = −9.52 m^2/s.

$[ReO_3(\eta^2\text{-}Tpm)(PTA)][ReO_4]$ (4). An equimolar amount of Tpm (60.2 mg, 0.206 mmol), and then a 2:1 molar amount of PTA (64.7 mg, 0.412 mmol) in MeOH, were added to a stirred solution of Re_2O_7 (100.0 mg, 0.206 mmol) in MeOH (10 mL). After ~10 min, a yellow solid precipitated from the blue solution. The solid was isolated by filtration, washed with 5 mL of methanol, and dried in vacuo. **4** is soluble in H_2O ($S_{25°C} \approx 1.88$ mg mL^{-1}). Yield = 38%, based on Re_2O_7. **4**, $C_{16}H_{22}N_9O_7PRe_2$ (855.8): Calcd. C 22.5, N 14.7, H 2.6; Found C 22.2, N 14.1, H 2.6. IR (KBr): 2954 [C–H, (Tpm)] cm^{-1}, 2917 [asym C–H, (CH_2) (PTA)], 2876 [sym C–H, (CH_2) (PTA)], 1641 [C=C, (Tpm)], 1516 [C=N, (Tpm)], 1414 [asym P–CH_2, (PTA)], 1309 [sym P–CH_2, (PTA)], 1292 [N–CH_2, (PTA)], 1243 [N–C–N, (PTA)], 1026 [N–C–N, (PTA)], 911 (Re=O). ^1H NMR (400 MHz, D_2O): δ 9.80 (s, br, 1H, $HC\text{-}(pz)_3$), 8.72 (s, br, 1H, pz-H3,5) 8.33 (s, br, 2H, pz-H3,5), 8.12 (s, br, 1H, pz-H3,5), 7.76 (s, br, 2H, pz-H3,5), 6.88 (s, br, 1H, pz-H4), 6.52 (s, br, 2H, pz-H4), 4.59 and 4.56 ($J(H^AH^B)$ = 13.5 Hz, 6H, NCH^AH^BN, PTA), 4.40 (s, 6H, PCH_2N, PTA). $^{13}C\{^1H\}$NMR (100 MHz, D_2O): 140.9 (s, pz-C3,5), 130.2 (s, pz-C3,5), 106.9 (s, pz-C4), 82.1 (s, $HC\text{-}(pz)_3$), 71.2 (s, NCH_2N), 46.90 (d, $^1J(CP)$ = 54.0 Hz, PCH_2N). $^{31}P\{^1H\}$NMR (162 MHz, D_2O): −68.2 (s).

$[ReO_3(Hpz)(HMT)][ReO_4]$ (5). A methanol solution (10 mL) of HMT (58.3 mg, 0.416 mmol) was added dropwise to a methanol solution (10 mL) of Re_2O_7 (100.0 mg, 0.206 mmol). An equimolar amount (relative to Re_2O_7) of LiTpms salt (60.4 mg, 0.206 mmol) was added. The reaction mixture was stirred overnight, the volume of the solution was reduced under vacuum, and then Et_2O was added. Slow evaporation of the solvent resulted in the formation of a brown compound (**5**). Yield = 40%, based on Re_2O_7. $C_9H_{16}N_6O_7Re_2$ (692.7): Calcd. C 15.6, N 12.1, H 2.3; Found C 15.3, N 11.7, H 2.8. IR (KBr): 3072 cm^{-1} [N–H, (Hpz)], 1669 and 1587 [C=C and N=C, (Hpz)], 1265 [C–N, (HMT)], 910 (Re=O). ^1H NMR (400 MHz, D_2O): δ 8.9 [s, 1H, H(1) Hpz], 7.9 [s, 1H, H(3) or H(5) Hpz], 7.7 [s, 1H,

H(3) or H(5) Hpz], 6.4 [s, 1H, H(4) Hpz], 4.6 [s, br, 6H, NCH_2N (HMT)], 4.4 (s, br, 6H, $N^{coord}CH_2N$ (HMT)). $^{13}C\{^1H\}$NMR (100 MHz, D_2O): 141.8 [s, C(3) Hpz], 130.6 [s, C(5) Hpz], 107.6 [s, C(4) Hpz]. 71.4 (s, NCH_2N, HMT).

[ReO(Tpms)(HMT)] ***(6)***. Li(Tpms) (61.8 mg, 0.206 mmol) was added to a methanolic solution of Re_2O_7 (100.0 mg, 0.206 mmol, 10 mL of MeOH). Then, a 2:1 molar amount of HMT (57.8 mg, 0.412 mmol) in MeOH was added. After stirring for ∼10 min, a yellow solid precipitated from the blue solution. The solid was isolated by filtration, washed with 5 mL of methanol and dried in vacuo. **6** is soluble in H_2O ($S_{25°C} \approx 15$ mg mL^{-1}). Yield = 35%, based on Re_2O_7. **6**, $C_{16}H_{21}N_{10}O_4ReS$ (635.7): Calcd. C 30.2; H 3.3; N 22.0; Found C 29.7, H 3.2, N 21.3. IR (KBr): 1515 cm^{-1} (C=C, Tpms), 1272 [C−N, (HMT), 918 (Re=O). ^1H NMR (400 MHz, D_2O): δ 7.89 (s, br, 3H, pz-H3,5), 7.67 (s, 3H, pz-H3,5), 6.41 (s, br, 3H, pz-H4), 4.61 (s, br, 6H, NCH_2N (HMT)), 4.44 (s, br, 6H, $N^{coord}CH_2N$ (HMT)). $^{13}C\{^1H\}$-NMR (100 MHz, D_2O): 141.0 (s, pz-C3,5), 130.0 (s, pz-C3,5), 107.0 (s, pz-C4), 81.6 (s, O_3SC-(pz)$_3$), 73.5 (s, NCH_2N).

[ReCl$_2${N$_2$C(O)Ph}(PTA)$_3$] ***(7)***. A 10:1 molar amount of PTA (208.5 mg, 1.33 mmol) was added to a stirred solution of $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$ (130.4 mg, 0.13 mmol) in toluene (25 mL). Then, the reaction mixture was refluxed during 3 h, yielding a reddish brown solid. The suspension was cooled to room temperature, the solid was isolated by filtration, and washed with MeOH (15 mL). **7** is soluble in H_2O ($S_{25°C} \approx 8$ mg mL^{-1}). Yield = 61%, based on $[ReCl_2(N_2COPh)(Hpz)(PPh_3)_2]$. **7**, $C_{25}H_{41}Cl_2N_{11}P_3ORe$ (861.7): Calcd C 34.8, N 17.9, H 4.9; Found C 35.1, N 17.8, H 5.1. IR (KBr): 2919 [m, C−H, (CH_2) (PTA)], 1627 [m, C=O, η^1-*N*−$N_2C(O)Ph$], 1579 [s, N=N, η^1−*N*−$N_2C(O)Ph$], 1449 [m, asym P−CH_2, (PTA)], 1383 [m, sym P−CH_2, (PTA)], 1284 [m, N−CH_2, (PTA)], 1016 and 1242 [m, N−C−N, (PTA)]. Far IR (polyethylene): 299 and 267 [s, ν(Re−Cl)]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 [d, 2H, J_{HH}= 5.4 Hz, *o*-H (Ph)], 7.58 [vt, 1H, *p*-H (Ph)], 7.40 [vt, 2H, *m*-H (Ph)], 4.67−4.37 (m, 24H, NCH_2N + PCH_2N (PTA)), 4.17 [s, 12H, PCH_2N (PTA)]. $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): −74.7 (t) and −84.8 (d), ^2J(PP) = 9.8 Hz.

Catalytic Studies. Under typical conditions, Re catalysts were used as stock solutions (for this, 10.0 mg of the compound were dissolved in 2.00 mL of 1,2-dichloroethane (1,2 DCE)). The required amount of this stock solution for the desired oxidant/catalyst molar ratio (1000:1) was transferred to a second flask containing 3.00 mL of 1,2-dichloroethane. Then, 1.7 mmol of H_2O_2 as a 30% aqueous solution (102 μL) and 1.7 mmol of substrate were added, and the reaction solution was stirred for 6 h at the desired temperature (typically 70 °C) and normal pressure (dinitrogen atmosphere). Then, 120 μL of cycloheptanone (internal standard) and 10.00 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The products were analyzed by GC using the internal standard method.

Computational Details. The full geometry optimization of all structures has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP)[63] with the help of the Gaussian 03[64] program package. Restricted approximations for the structures with closed electron shells and unrestricted methods for the structures with open electron shells have been employed. No symmetry operations have been applied. The geometry optimization was carried out using a quasi-relativistic Stuttgart pseudopotential that described 60 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d][65] for the Re atom and the 6-31G(d) basis set for other atoms. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C.

Total energies corrected for solvent effects (E_s) were estimated at the single-point calculations on the basis of gas-phase geometries using the polarizable continuum model in the CPCM version[66] with MeOH as a solvent. The solvent effects for the calculations of the bond energies in **2P** and **2N** were estimated at the CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d) level of theory. The UAKS model was applied for the molecular cavity. The entropic term in MeOH solution (S_s) was computed according to the procedure described by Wertz[67] and Cooper and Ziegler[68] (see the Supporting Information for details). The enthalpies and Gibbs free energies in solution (H_s and G_s, respectively) were estimated using expressions 1 and 2:

$$H_s = E_s + H_g - E_g \tag{1}$$

$$G_s = H_s - TS_s \tag{2}$$

where E_s and E_g are the total energies in solution and in gas phase, respectively, and H_g is the gas-phase enthalpy calculated at the corresponding level.

The chemical potential (μ) and global softness (S) of the ReO_3^+ and $mPTA^+$ species were calculated using eqs 3 and 4:[69]

$$\mu \approx -\frac{I + A}{2} \tag{3}$$

$$S \approx \frac{1}{I - A} \tag{4}$$

where *I* and *A* are the vertical ionization potential and electron affinity, respectively. Fukui functions of atom *x* in a molecule with N electrons, f_x^+ and f_x^- (the former representing nucleophilic attack and the latter representing electrophilic attack), were defined in a finite-difference approximation using eqs 5 and 6:

$$f_x^+ = [q_x(N + 1) - q_x(N)] \tag{5}$$

$$f_x^- = [q_x(N) - q_x(N - 1)] \tag{6}$$

where q_x is the NBO electronic population of atom *x* in a molecule. The local atomic softnesses s_x^+ and s_x^- were calculated by the formulas listed as eq 7:

$$s_x^+ = f_x^+ S \quad \text{and} \quad s_x^- = f_x^- S \tag{7}$$

The total energies of the interaction between the ReO_3^+ and $mPTA^+$ fragments (ΔE_{int}) were calculated with the help of the HSAB formalism,[69,70] using the expression depicted in eq 8:

$$\begin{aligned}\Delta E_{int} &= \Delta E_\nu + \Delta E_\mu \\ &= -\frac{1}{2}\left[\frac{(\mu_{ReO_3^+} - \mu_{mPTA^+})^2}{s_{Re}^+ + s_x^-}\right] s_{Re}^+ s_x^- - \frac{1}{4}\left(\frac{\lambda}{s_{Re}^+ + s_x^-}\right)\end{aligned} \tag{8}$$

where ΔE_ν and ΔE_μ are the components of ΔE_{int} at the constant external potential and chemical potential, respectively, *x* is an atom of $mPTA^+$ interacting with Re (P or N), λ is a parameter estimated by eq 9

$$\lambda = \left|\sum_{x=1}^{4} q^{eq}_{x,ReO_3^+} - \sum_{x=1}^{4} q^{\circ}_{x,ReO_3^+}\right| \tag{9}$$

where q_x^{eq} and q_x° are the NBO electronic populations of atom *x* of the ReO_3^+ fragment in the **2P** or **2N** molecule at equilibrium (the first term) and in the isolated optimized ReO_3^+ molecule (the second term).

3. RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes. Reactions of Re_2O_7, in MeOH at room temperature, with the water-soluble aminophosphine PTA, its derivative [Me-PTA]I, its N-analogous HMT, or PTA in the presence of the neutral Tpm, led to new water-soluble and stable trioxo-rhenium(VII) complexes $[ReO_3(PTA)_2][ReO_4]$ (**1**), $[ReO_3(mPTA)][ReO_4]I$ (**2**), $[ReO_3(HMT)_2][ReO_4]$ (**3**), and $[ReO_3(\eta^2\text{-}Tpm)(PTA)][ReO_4]$ (**4**), respectively, whereas the oxo-complexes $[ReO_3(Hpz)(HMT)][ReO_4]$ (**5**) and [ReO(Tpms)(HMT)] (**6**) were obtained in the presence of HMT and the water-soluble Li(Tpms) salt (recall Scheme 1). The formation of the latter complexes (**5** and **6**) was found to be very sensitive to the sequence of reagent additions (see the Experimental Section). Moreover, the formation of **5** involves the rupture of a C(sp^3)−N(pyrazolyl) bond in $Tpms^-$. Other cases of metal-induced cleavage of such a type of bond have been reported, namely, the C−N bond rupture in $HC(pz)_3$ or $HC(3,5\text{-}Me_2pz)_3$ by the benzoylhydrazido rhenium(V) chelate $[ReCl_2\{\eta^2\text{-}N,O\text{-}N_2C(O)Ph\}(PPh_3)_2]$,[28b] in $HC(3,5\text{-}Me_2pz)_3$ by triethyl vanadate to form $[VO_2(3,5\text{-}Me_2Hpz)_3][BF_4]$[28j] or in bis(pyrazolyl)propane $(CH_3)_2C(pz)_2$ by Pt(II) complexes,[71] e.g., $[PtCl_2(RCN)_2]$ (R = Me or Ph) or $K_2[PtCl_4]$. In all of the reported cases, the way the cleavage reaction occurs has not been established, but can possibly involve metal-promoted hydrolysis of $Tpms^-$.[28a]

The benzoyldiazenido PTA complex $[ReCl_2\{N_2C(O)Ph\}(PTA)_3]$ (**7**) was prepared by ligand exchange at $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$, in a 1:10 metal to PTA molar ratio, in hot toluene (Scheme 2). For a lower amount of PTA (e.g., 1, 2, or 5 mol equiv), replacement of the PPh_3 or Hpz ligands by PTA did not occur. The use of more polar solvents, namely, CH_2Cl_2 and MeOH, led to the formation of the phosphine oxide (PTA═O).

The obtained complexes were characterized by IR and NMR spectroscopies, elemental analysis, and electrochemical study.

The IR spectra of **1**, **2**, **4**, and **7** show typical bands of coordinated PTA (or coordinated $[mPTA]^+$ for **2**), in the 2919−2880 and 2876−2874 cm^{-1} ranges assigned to $\nu_{as}[C-H(CH_2)]$ and $\nu_s[C-H(CH_2)]$; in the 1452−1416, 1383−1309 and 1292−1284 cm^{-1} ranges, attributed to $\nu_s(P-CH_2)$, $\nu_{as}(P-CH_2)$ and $\nu(N-CH_2)$, respectively; and in the 1026−1014 cm^{-1} and 1250−1242 cm^{-1} ranges attributed to ν(NCN). For **7**, the presence of the chloride ligands is confirmed by the strong intensity ν(Re−Cl) bands at 299 and 267 cm^{-1}. Moreover, **7** exhibits strong bands at 1627 and 1579 cm^{-1} assigned to ν(C═O) and ν(N═N), respectively, of the benzoyldiazenido ligand. Such IR bands for η^1-*N*-NNC(O)Ph ligand appear at comparable values for the parent benzoyldiazenido-Re(III) pyrazole complex $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$[28b] [$\nu$(C═O) 1593 and ν(N═N) 1565 cm^{-1}]. The benzoyldiazenido ligand is expected to behave as a 3-electron donor (allowing the 18-electron configuration to be achieved by the complex) and thus to present the linear coordination geometry $RE\leftrightharpoons N{=}NC(O)Ph$.[28b,72]

Complexes **1**−**6** exhibit, in their IR spectra, a strong and broad ν(Re═O) band at ~910 cm^{-1} (less intense for **6** due to the lower number of Re═O bonds), the ν(CH) of the methine moiety of the hydrotris(pyrazol-1-yl)methane ligand (for **4**), the ν(S═O) of the methanesulfonate group (for **6**), the ν(C═C) and ν(C═N) of the pyrazolyl rings at normal ranges (for **4** and **6**) or the typical bands of a tertiary amine, concerning the HMT ligand (for **3**, **5**, and **6**).

In the $^{31}P\{^1H\}$ NMR spectrum of **1**, the singlet at $\delta = -70.1$ is consistent with the Re metal center bearing two PTA ligands in the axial positions. **2** displays, in its ^1H NMR spectrum, four types of methylene groups of the $[mPTA]^+$ cationic ligand: NCH_2N, NCH_2N^+, and PCH_2N are all of AB type. For PCH_2N^+, a singlet has been observed. The ^1H NMR spectra of $[ReO_3(HMT)_2][ReO_4]$ (**4**), $[ReO_3(Hpz)(HMT)][ReO_4]$ (**5**) and [ReO(Tpms)(HMT)] (**6**) show two types of methylene groups of coordinated HMT, $N-CH_2-N$ and $N^{coord}-CH_2-N$, in contrast to the free ligand, which exhibits only one resonance at δ 4.54. The coordination of one pyrazole ring at **5** is evidenced by the appearance of three singlets at δ 7.89, 7.66, and 6.41 (each integrated for one proton, corresponding to the 3, 4, and 5 position, respectively, in the pyrazole ring) and at 8.96, the signal attributed to the NH proton. A similar pattern was observed for the Re(III) pyrazole complex $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$.[28b] The equivalence of the pyrazolyl groups in **6** is indicated by both ^1H and $^{13}C\{^1H\}$ NMR spectra which display a single resonance for each type of proton or carbon, respectively, i.e., for the 3, 4, or 5 position in the ring. However, in **4**, those groups, as expected, are nonequivalent.

The ^1H NMR spectrum of **7** exhibits the expected resonances of the *ortho*-, *meta*-, and *para*-protons of the phenyl ring of the benzoyldiazenido ligand. In addition, ^1H NMR spectrum shows a set of resonances in the range δ 4.67−4.17 for $N-CH_2-N$ and $P-CH_2-N$ methylene of coordinated PTA ligands with a ratio of 1:2, and the $^{31}P\{^1H\}$ NMR spectrum consists of two signals: triplet at δ −74.7 and doublet at −84.8 ($^2J_{PP}$ = 9.8 Hz). This is indicative of a meridional octahedral complex (recall Scheme 2). The resonances are comparable to those observed for $[RuI_2(H_2O)(mPTA)_3]I_3\cdot 2H_2O$.[8c]

The $^{31}P\{^1H\}$ spectra of Re complexes bearing PTA or $[mPTA]^+$ exhibit coordination through P atoms to the metal center, resulting in downfield shifts of $^{31}P\{^1H\}$ resonances upon coordination. The ^1H NMR spectra confirm the *P*-coordination modes. $P-CH_2-N$ for **1** and **4** and $P\text{-}CH_2-N^+$ methylene protons for **2** occur as singlets, although for free PTA or $[mPTA]^+$ they give doublets (^2J(PH) = 10.5 and 6.5 Hz, respectively).[8c,d] On the other hand, in the case of coordination through only the N atoms of the adamantane cage to the metal center, similar spectra to those of the free ligands would be expected, e.g., as reported previously[73] for the $^{31}P\{^1H\}$ and ^1H NMR spectra of $[ZnCl_2(PTA)_2]$ (its structure was confirmed by X-ray analysis) with PTA coordinated through only a N atom.

In addition, although PTA and HMT are able to be polycoordinated, PTA compounds (**1**, **2**, **4**, and **7**) are expected to be monomeric, since we observed (see below) that the coordination of PTA to both Re(VII) and Re(III) centers by the P atom is clearly more preferable than the coordination by the N atom. Pulse-field-gradient spin−echo NMR, which relies on differences in diffusion coefficients of molecules with different sizes in solution (see the Experimental Section and Figure S8 in the Supporting Information),[74] has been used in the analysis of **3**, as a HMT representative case, and excluded the formation of polycoordinated species. The average value of the diffusion coefficient ($D = 3.0 \times 10^{-10}\ m^2\ s^{-1}$) of **3** is in accord with a monomeric form of the complex in solution. In fact, the coordination sphere seems to be saturated around of metal centers in **1**−**7**; therefore, we postulated the formation of monomeric form of oxorhenium complexes, especially in solution.

Electrochemical Behavior of 1−7. Complexes **1**−**5** exhibit, by cyclic voltammetry (CV), at a platinum electrode at 25 °C in a 0.2 M $[^nBu_4N][BF_4]$/DMSO solution, a reduction wave at potential values in the range from −0.31 V to −0.84 V vs. SCE (see Figures S1−S5 in the Supporting Information) assigned[28a,75] to the Re(VII) → Re(VI) reduction and comparable to that reported[28a] for the related $[ReO_3(Tpms)]$ ($^IE_{1/2}^{red}$ = −0.83 V vs. SCE). (See Table 1.) For **2** and **3**, at a lower potential, a second reduction is observed at $^{II}E_p^{red}$ = −0.81 and −1.12 V vs SCE, respectively. Neither a metal-centered oxidation nor a ligand-centered oxidation was detected for **1**−**5**, the former being in accordance with the

Table 1. Cyclic Voltammetric Data[a] for $[ReO_3(PTA)_2][ReO_4]$ (1), $[ReO_3(mPTA)][ReO_4]I$ (2), $[ReO_3(HMT)_2][ReO_4]$ (3), $[ReO_3(\eta^2\text{-Tpm})(PTA)][ReO_4]$ (4), $[ReO_3(Hpz)(HMT)][ReO_4]$ (5), $[ReO(Tpms)(HMT)]$ (6), and $[ReCl_2\{N_2C(O)Ph\}(PTA)_3]$ (7)

complex	${}^{I}E_p^{red}$ ($E_{1/2}^{red}$)	${}^{II}E_p^{red}$ ($E_{1/2}^{red}$)	${}^{I}E_p^{ox}$ ($E_{1/2}^{ox}$)	${}^{II}E_p^{ox}$ ($E_{1/2}^{ox}$)
1	(−0.65)			
2[b]	(−0.31)	(−0.81)	0.56	(0.84)
3	(−0.84)	−1.12		
4	(−0.62)			
5	(−0.33)			
6	−0.83		(0.86)	1.44
7	−1.56		(0.78)	1.67

[a] Values given in units of V ± 0.02 relative to SCE (see Experimental Section); scan rate of 200 mV s^{-1}. Values for reversible waves are given in parentheses. [b] The two observed oxidation waves are due to iodide oxidation.

metal d^0 Re(VII) electron count. Moreover, the $[ReO_4]^-$ counterion is also redox inactive in the studied potential range. For **2**, two oxidation waves are observed at ${}^{I}E_p^{ox}$ = 0.56 and ${}^{I}E_{1/2}^{ox}$ = 0.84 V vs SCE, which are assigned to the oxidation of the iodide counterion.

The Re(III) complexes **6** and **7** exhibit a single-electron irreversible reduction wave at ${}^{I}E_p^{red}$ = −0.83 and −1.56 V vs SCE, respectively (see Figures S6 and S7 in the Supporting Information), assigned to the Re(III) → Re(II) reduction.[28a] Moreover, a first single-electron partially reversible oxidation wave at ${}^{I}E_{1/2}^{ox}$ = 0.86 V (**6**) and 0.78 V (**7**) vs SCE is assigned to the Re(III) → Re(IV) oxidation,[28a] which is followed, at a higher potential, by a second irreversible one at ${}^{II}E_p^{ox}$ = 1.44 and 1.67 V, respectively, assigned to the Re(IV) → Re(V) oxidation.[28a]

Complex **7** and its parent pyrazole triphenylphosphine complex $[ReCl_2\{N_2C(O)Ph\}(Hpz)(PPh_3)_2]$[28b] display comparable reduction potentials, what is indicative of an overall electron-donor character of the three PTA ligands in **7** comparable to that of the pyrazole and two PPh_3 ligands in the latter complex, in accordance with the values of the electrochemical Lever parameter E_L (the stronger the character of E_L, the lower the E_L value) for these ligands (0.34 V,[76] 0.20 V,[77] and 0.39 V[77] vs NHE, respectively). In fact, $\Sigma E_L(3\ \text{PTA})$ = 1.02 ≅ $\Sigma E_L(\text{Hpz} + 2\ PPh_3)$ = 0.98 V vs NHE. However, one should be cautious since an accurate comparison cannot be established, because the reduction potential is not the thermodynamic one in view of the irreversibility of the reduction wave.

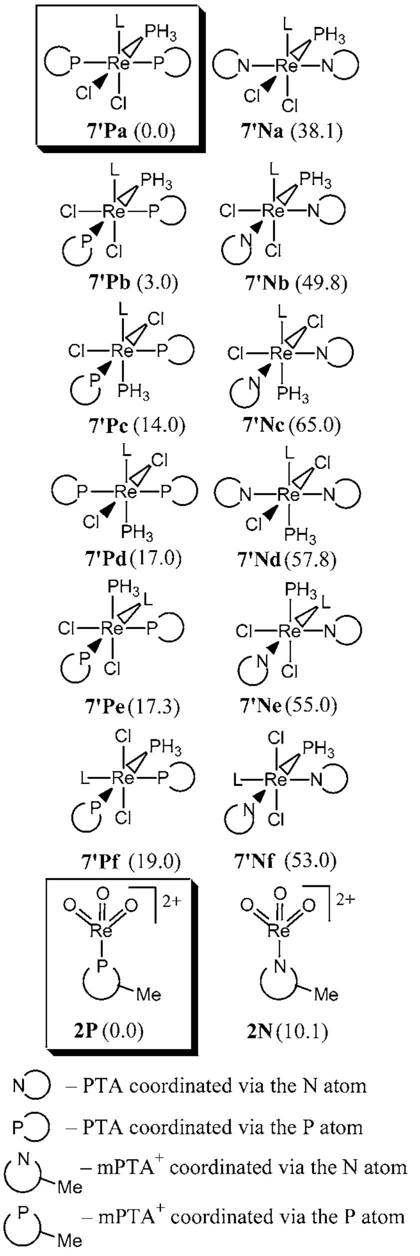


Figure 2. Calculated structures for complexes of types **2** and **7** with relative ΔG_s values indicated (given in kcal/mol). P◯ and N◯ denote PTA coordinated via the P and N atom, respectively; L = N═NC(═O)Me. The most thermodynamically stable ones are highlighted.

Theoretical Considerations. The PTA ligand has two types of donor atoms (P and N atoms) able to coordinate to a metal. Complexes with such coordination modes of PTA, i.e., via P,[28i,29,76,78] via N,[79] or both[80] are known. With the aim to investigate the thermodynamic preferences of the PTA coordination to Re(VII) and Re(III) in the studied complexes, quantum-chemical calculations at the B3LYP level of theory have been carried out for complex **2** (see **2P** and **2N**, Figure 2) and the 7 model species (**7′Pa-f** and **7′Na-f**; see Figure 2). The results indicate that all structures with the PTA coordinated via the P atom are more stable than the corresponding N-PTA coordinated structures by 10.1−51.0 kcal/mol (Figure 2). This is taken into account by a higher stability of the $Re-P_{PTA}$ bond, compared to the $Re-N_{PTA}$ one. Indeed, the calculated $Re-P_{PTA}$ bond energy in **2P** for the MeOH solution (19.5 kcal/mol) is significantly higher than the $Re-N_{PTA}$ energy in **2N** (8.0 kcal/mol).

These results may be interpreted in terms of the hard−soft acid−base (HSAB) theory. The calculations indicate that the Re atom in ReO_3^+ is a rather soft center, which is taken into account by the significant value of its f^+ Fukui function, which is comparable with the f^- value of the P atom in $mPTA^+$, and by the high global softness of ReO_3^+ (see Table 2). (An additional discussion is given in the Supporting Information.) Hence, the interaction of the relatively soft Re center with the soft P atom of PTA should be more preferable than that with the much-harder N atom. The quantum-chemical calculations using the HSAB formalism (see Computational Details) indicate that both terms of the Re−PTA interaction energy (ΔE_ν and ΔE_μ)

Table 2. Calculated Vertical Ionization Potentials and Electron Affinities, Chemical Potentials (μ), Global (S) and Local (s^+ and s^-) Softnesses, Fukui Functions (f^+ and f^-), λ Parameter, ΔE_ν, ΔE_μ, and Total (ΔE_{int}) Interaction Energies

	ReO$_3^+$	mPTA$^+$	
vertical ionization potential, I	0.697	0.451	
vertical electron affinity, A	0.377	0.057	
chemical potential, μ	−0.537	−0.254	
global softness, S	3.130	2.539	
	Re in ReO$_3^+$	P in mPTA$^+$	N in mPTA$^+$
f^+	0.350		
s^+	1.095		
f^-		0.358	0.126
s^-		0.908	0.320
	Re−P in **2P**	Re−N in **2N**	
λ	0.616 au	0.403 au	
ΔE_ν	−12.48 kcal/mol	−6.22 kcal/mol	
ΔE_μ	−48.27 kcal/mol	−44.66 kcal/mol	
ΔE_{int}	−60.75 kcal/mol	−50.88 kcal/mol	

and, hence, the total interaction energy (ΔE_{int}) are significantly higher for the Re−P_{PTA} bond than for the Re−N_{PTA} one (see Table 2). The higher negative ΔE_ν value for the Re−P bond is taken into account by the much-higher local softness s^- of the P atom in PTA, compared to the N atom (0.908 hartree^{-1} vs 0.320 hartree^{-1}). In the case of the ΔE_μ term, its more-negative value for the Re−P bond is determined by the PTA → Re charge transfer [the λ parameter, see eq 9] which is also higher in **2P** than in **2N**.

Among the possible geometrical isomers of **7′P** and **7′N**, the most thermodynamically stable ones are **7′Pa** and **7′Na** although isomer **7′Pb** is only 3.0 kcal/mol less stable than **7′Pa**.

Application of the New Re Complexes as Catalysts for Baeyer−Villiger Oxidations of Cyclic and Acyclic Ketones. We found that the oxo-rhenium complexes **1**−**6** (recall Scheme 1) can exhibit a remarkable catalytic activity (e.g., turnover numbers, TONs, up to ~9 × 10^3 moles of product per mole of Re catalyst, for **1**), under relatively mild conditions for the partial oxidation of different simple cyclic (2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone, cyclobutanone) and acyclic (pinacolone) ketones to the respective lactones and esters, in a single-pot process (see Scheme 3 and Table 3, as we as Figure S1 in the Supporting Information and Figure 3). The catalytic systems are based on the above-described oxo-Re compounds **1**−**6**, using hydrogen peroxide (30% aqueous solution) as the oxidizing agent and 1,2-dichloroethane (1,2 DCE) as the solvent, under a typical temperature of 70 °C and a reaction time of 6 h. 1,2 DCE was chosen as the typical solvent for our systems, because of its high resistance to oxidizing agents and also in view of the good solubility of both catalysts and substrates. It has also been used in other cases as the most appropriate solvent for BV oxidations.[81]

In general, the tested Re(VII or III) complexes exhibit higher activities than the simple rhenium oxides K[$\mathrm{ReO_4}$] (Table 3, entries 9, 15, 26, 30 and 34) or $\mathrm{Re_2O_7}$[57] (Table 3, entries 10, 16, 21 and 35). The oxo-Re(VII) PTA or m-PTA complexes, *i.e.*, [$\mathrm{ReO_3(PTA)_2}$][$\mathrm{ReO_4}$] (**1**) and [$\mathrm{ReO_3}$(mPTA)][$\mathrm{ReO_4}$]I (**2**), provide the most active catalysts under the conditions of this study for the oxidation of all tested ketones. Moreover, in the presence of **1** or **2**, the BV oxidation of the acyclic pinacolone to *tert*-butylacetate proceeds very effectively, exhibiting much higher yields (up to 34% for **1**, Table 3, entry 31) than the highest previously observed[57] value (12%, by using the chloro-Re(III) scorpionate complex [$\mathrm{ReCl_3}$(Tpm)]). For the cyclic ketones, the achieved yields are comparable with those exhibited[57] by the Re(V) complex [$\mathrm{ReCl_2}\{\eta^2\text{-}N,O\text{-}\mathrm{C(O)Ph}\}\mathrm{(PPh_3)_2}$] (e.g., 42%, 27%, 14% or 45% for 2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone or cyclobutanone, respectively), the most active of a series of Re(III−V) complexes bearing *N*- or oxo-ligands. The reported yields of the [$\mathrm{(CH_3)ReO_3}$]/$\mathrm{H_2O_2}$ catalyzed BV oxidation of cyclic ketones in ionic liquids (up to 98% and 70% for cyclobutanone and cyclopentanone, respectively)[20] are higher than those obtained in our Re catalytic systems, but for the 6-membered ring ketones, such as cyclohexanone and 2-methylcyclohexanone, we have achieved comparable or even better results. The obtained yields in the present work are also commonly comparable to those observed for phosphinic Pt(II) complexes.[38,39]

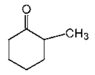
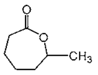
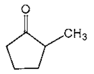
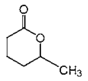
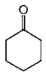
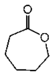
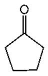
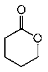
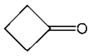
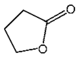
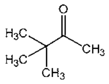
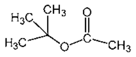
No direct relationship of the activity with the reduction potential (see above) is observed, in contrast to what was shown[38a] for series of closely related platinum(II)-diphosphine complexes of the types [Pt(μ-OH)(LL)]$_2$[$\mathrm{BF_4}$]$_2$ (LL = organodiphosphine or fluoro-substituted derivative) and [Pt($\mathrm{OH_2}$)$_2$(LL)](OTf)$_2$, where the activity followed the Lewis acidity of the metal center. However, such a lack of correlation for the Re complexes of the present study is not surprising since, in general, they are not so closely related as those of the above series of Pt(II) compounds, and also in view of the irreversible character of the reduction waves, their reduction potentials thus being not the thermodynamic ones and depending also on kinetic factors. In addition, steric factors can also play a role.

Because of the proposed mechanistic pathway for MTO-catalyzed BV oxidation,[20,41,42,82] the reaction can proceed via the formation of active peroxo-Re species derived from the starting complexes in the presence of $\mathrm{H_2O_2}$, which would attack the electrophilic carbon of the carbonyl group of the ketone ligand. Complete regioselectivity was observed in our case for all BV oxidations of unsymmetrical ketones, 2-methylcyclopentanone, 2-methylcyclohexanone, and pinacolone, to afford δ-hexalactone, 6-methylhexanolide, or *tert*-butylacetate, respectively, as a result of the formal insertion of the O atom between the carbonyl and the more-substituted C_α atom. The alkyl substituent at C_α of the ketone promotes the migration of the substituted side of the ketone as a carbanion to the peroxo-atom.[48] Other cases of complete regioselectivity have also been reported in some other metal catalytic systems.[38b,39,83]

Effect of the Oxidant-to-Catalyst Molar Ratio. The influence of the peroxide-to-catalyst molar ratio was studied for the BV oxidation of 2-methylcyclohexanone and 3,3-dimethyl-2-butanone (pinacolone) in the presence of **1** (see Figure 3 and Table S1 in the Supporting Information). The increase of the $n(\mathrm{H_2O_2})/n(\text{catalyst})$ molar ratio, by decreasing the catalyst amount, results in higher TONs, e.g., the TON for the oxidation of the former ketone in the presence of complex **1** is enhanced from 40 to 9.14 × 10^3 (see Table S1 in the Supporting Information, entries 1 and 5, respectively) upon changing that ratio from 100 to 40 × 10^3. However, the yield values decline after reaching a maximum, because of deceleration of the reaction rate upon reducing the catalyst concentration.

Effect of the Reaction Time, Temperature, and Type of Solvent. The effect of the reaction time was studied for

Table 3. Baeyer–Villiger (BV) Oxidation of Several Ketones Catalyzed by Re Complexes 1–6 (Selected Data)[a]

Entry	Substrate	Catalyst	Yield (%)[b]	TON[c]	Conv.[d]	Select.[e]	Product
1		**1**	30	307	66	45	
2[f]		**1**	30	298	94	32	
3[g]		**1**	2	21	62	3	
4		**2**	31	307	85	36	
5		**3**	15	148	68	22	
6		**4**	16	161	75	21	
7		**5**	11	108	67	16	
8		**6**	9	89	70	10	
9		$K[ReO_4]$	15	147	42	35	
10[h]		Re_2O_7	7	67	60	11	
11		**1**	25	254	51	49	
12[i]		**1**	21	211	90	24	
13		**2**	22	222	57	39	
14		**4**	13	127	42	31	
15		$K[ReO_4]$	17	170	55	49	
16[h]		Re_2O_7	10	104	26	40	
17		**1**	18	180	59	20	
18[j]		**1**	4	42	21	19	
19		**2**	16	162	37	43	
20		**4**	10	102	38	26	
21[h]		Re_2O_7	3	27	55	5	
22		**1**	26	254	63	37	
23[i]		**1**	23	230	95	24	
24		**2**	34	341	58	41	
25		**4**	34	340	67	51	
26		$K[ReO_4]$	17	170	33	51	
27		**1**	26	254	90	29	
28[k]		**2**	27	276	89	30	
29		**4**	36	363	100	36	
30		$K[ReO_4]$	15	153	100	15	
31		**1**	34	335	87	39	
32		**2**	21	205	84	25	
33		**4**	7	66	89	11	
34		$K[ReO_4]$	12	119	54	22	
35[h]		Re_2O_7	2	18	51	4	

[a] Reaction conditions (unless stated otherwise): rhenium catalyst (1.7 μmol, used as a stock solution in 1,2-dichloroethane), 1.7 mmol of substrate, H_2O_2 (1.7 mmol, i.e. 1000:1 molar ratio of oxidant to Re catalyst), 1,2-dichloroethane (3.0 mL), 6 h, 70 °C, under dinitrogen. Yield and TON determined by GC analysis. [b] Molar yield (%) based on the ketone substrate, i.e., number of moles of lactone (or ester) per 100 moles of ketone. [c] TON = turnover number (number of moles of product per mole of Re catalyst). [d] Moles of converted (reacted) substrate per mole of substrate. [e] Moles of lactone (or ester) per mole of converted substrate. [f] Oxidant/substrate =2:1. [g] Oxidant/substrate =4:1. [h] For comparative purposes.[57] [i] 4 days. [j] In the presence of acid, $n(HNO_3)$ /n(substrate) = 10. [k] Reaction time = 0.25 h.

complex **2** using 2-methylcyclohexanone and cyclobutanone (see Figure 4 and Table S2 in the Supporting Information). For the former substrate, the lactone yield and TON increase during the first 6 h, achieving maximum values (31% and 307, respectively) before dropping slightly, which was conceivably due to product overoxidation or hydrolysis.[84] In the case of cyclobutanone, a lactone yield of ~27% and a TON of 276 are achieved after only 0.25 h, while for the larger ring ketones no significant reaction is observed in the first 2–3 h, which is consistent with the known higher reactivity of the 4-membered ring ketone.

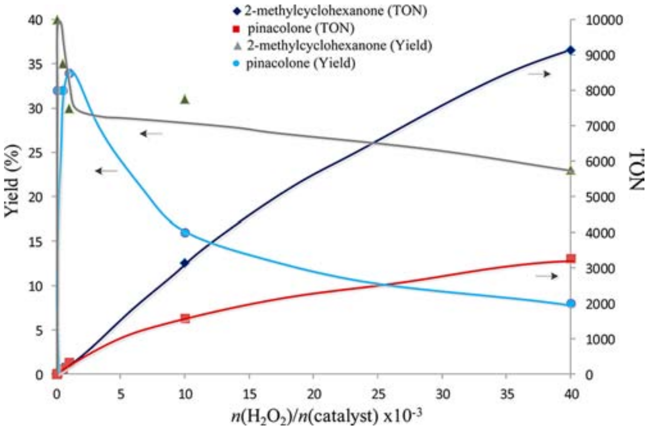


Figure 3. Effect of H_2O_2 relative amount (H_2O_2/catalyst molar ratio) on TON and yield (mol %, based on substrate) in the BV oxidation of 2-methylcyclohexanone [(black diamond, ◆) and (gray triangle, ▲)] and pinacolone [(red square, ■) and (●)], catalyzed by $[ReO_3(PTA)_2][ReO_4]$ (**1**). Reaction conditions are the same as those of the entries in Table S1 of the Supporting Information.

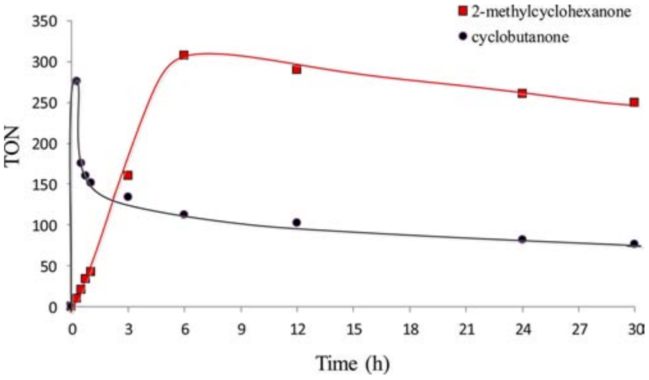


Figure 4. Effect of the reaction time on TON in the BV oxidation of 2-methylcyclohexanone (red squares, ■) and cyclobutanone (black circles, ●), catalyzed by $[ReO_3(mPTA)][ReO_4]I$ (**2**). Reaction conditions are the same as those of the entries for Table S2 in the Supporting Information.

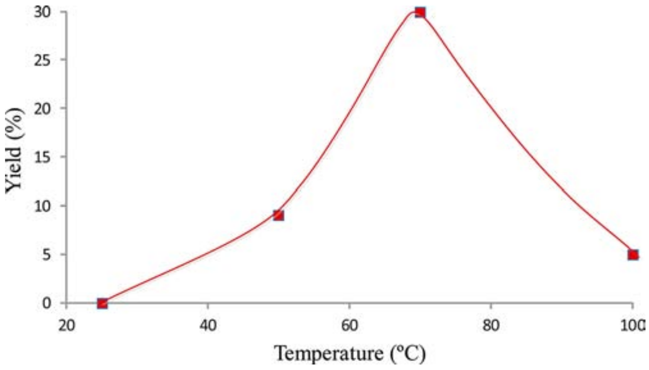


Figure 5. Effect of the temperature on lactone yield (mol %, based on substrate) in the BV oxidation of 2-methylcyclohexanone (red square, ■), catalyzed by $[ReO_3(PTA)_2][ReO_4]$ (**1**). Reaction conditions: catalyst (1.7 μmol), substrate, H_2O_2 (1.7 mmol) 1,2-dichloroethane (3.0 mL), 6 h, under dinitrogen.

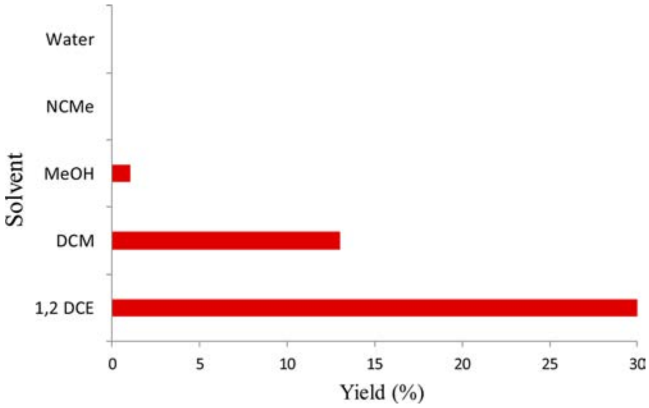


Figure 6. Effect of the type of solvent on lactone yield (mol %, based on substrate) in the BV oxidation of 2-methylcyclohexanone, catalyzed by $[ReO_3(PTA)_2][ReO_4]$ (**1**). Reaction conditions: catalyst (1.7 μmol), substrate, H_2O_2 (1.7 mmol) solvent (3.0 mL), 6 h, 70 °C, under dinitrogen. DCM = dichloromethane; 1,2 DCE = 1,2-dichloroethane.

The temperature is also an important factor and 70 °C appears to be the most adequate value for the cyclic ketone oxidation. In fact, e.g., we failed the attempt of performing the oxidation of 2-methylcyclohexanone in the presence of **1** at room temperature, whereas the use of 50 °C resulted in an important lactone yield reduction, relative to that at 70 °C (from 30% at 70 °C to 9% at 50 °C; see Figure 5). The lactone yield decreases above 70 °C, conceivably because of acceleration of the decomposition of the oxidant H_2O_2 and of any peroxo intermediates.[54,57]

Replacement of 1,2-dichloroethane (1,2 DCE) by other solvents resulted in a decrease of activity. In the case of the 2-methylcyclohexanone oxidation in the presence of **1**, the product yield was drastically reduced, from 30% (entry 1, Table 3) in 1,2 DCE to 13% in dichloromethane (DCM) or 1% in methanol (see Figure 6). Moreover, the use of acetonitrile or water results in a full inhibiting effect.

■ CONCLUSIONS

A series of water-soluble and stable oxo-rhenium(VII or III) complexes bearing the hydrosoluble phosphines PTA or m-PTA, the related cagelike tetra-amino HMT, or the C-scorpionates Tpm or Tpms, has been easily synthesized using Re_2O_7 as a convenient starting material. Moreover, ligand exchange at an organodiazenido diphosphinic Re(III) complex also leads to a water-soluble product, a Re(III) complex bearing three PTA ligands. Theoretical calculations at the density functional theory (DFT) level of theory indicated that the coordination of PTA to both Re(VII) and Re(III) centers by the P atom is clearly more preferable than the coordination by the N atom. This effect is taken into account by a higher stability of the Re−P_{PTA} bond, compared to the Re−N_{PTA} one, and also may be interpreted in terms of the HSAB formalism.

The new oxo-rhenium(VII or III) complexes exhibit a high activity toward the mild ketone oxidation with H_2O_2, leading to good yields of lactones and esters, with remarkably high TONs. The above ligands are expected to allow coordinative unsaturation at the metal, in view of their lability, and/or to promote proton-transfer steps, in view of their basic character; these are features that are favorable[28e−h,j,54−56,85] toward the occurrence of oxidation catalysis with H_2O_2. Moreover, the hydrosolubility of the complexes, together with the mild operation conditions, are particularly significant, in terms of developing green catalytic processes for ketone oxidations. The work also establishes that oxo-rhenium complexes bearing hydrosoluble PTA or C-scorpionate-type ligands, such as tris(pyrazolyl)methane or derivatives, are rather promising catalyst precursors for such a purpose, and deserve to be explored further.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes

The authors declare no competing financial interest.

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