

Developing the Kharasch Reaction in Aqueous Media: Dinuclear Group 8 and 9 Catalysts Containing the Bridging Cage Ligand Tris(1,2-dimethylhydrazino)-diphosphane

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Dedicated to Prof. José Gimeno on the occasion of his 60th birthday

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The dinuclear complexes $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$ (**4**) and $[\{\text{MCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ [$\text{M} = \text{Rh}$ (**5**), Ir (**6**)], containing the bridging cage-type ligand tris(1,2-dimethylhydrazino)diphosphane (THDP), have been synthesized in high yields (89–95 %) by treatment of dimers $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-}p\text{-cymene})\}_2]$ (**1**) and $[\{\text{M}(\mu\text{-Cl})(\eta^4\text{-cod})\}_2]$ [$\text{M} = \text{Rh}$ (**2**), Ir (**3**)] with one equivalent of THDP. The structure of the $(\eta^6\text{-arene})\text{-ruthenium(II)}$ derivative **4** has been unequivocally confirmed

by means of X-ray diffraction methods. All these complexes have been found to be active catalysts for the atom-transfer radical addition of bromotrichloromethane to olefins (Kharasch reaction) in heterogeneous aqueous media under mild conditions (room temp.).

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Introduction

A crucial factor in realizing a “green” chemical process involves the choice of a safe, non-toxic, and cheap solvent.^[1] In this context, the development of organic transformations in aqueous media has become one of the major cornerstones in modern chemistry.^[2] Following this general trend, there has been growing interest in the design of novel transition-metal catalysts for organic reactions in water in recent years,^[3] disclosing a wide variety of highly efficient and selective synthetic approaches.^[2,3]

The introduction of hydrophilic ligands into the coordination sphere of a transition metal is probably the most popular method for the preparation of water-soluble catalysts.^[3] Thus, a wide variety of functionalized phosphane ligands containing highly polar sulfonated, hydroxyalkyl, ammonium, phosphonium, carboxylate, carbohydrate, or phosphonate groups are known and their effectiveness in

aqueous-phase catalysis largely demonstrated.^[2,3] During the last decade, the cage-like water-soluble phosphane 1,3,5-triaza-7-phosphaadamantane (PTA; see Figure 1)^[4] has also received increasing attention and several ruthenium, rhodium, and palladium PTA complexes have been shown to be promising catalysts in aqueous media.^[5] In this context, we have recently reported that the structurally related trihydrazinophosphaadamantane ligand (THPA; see Figure 1)^[6] is also a suitable ligand for the solubilization of transition-metal catalysts in water.^[7] In particular, several water-soluble Ru^{II} , Rh^{I} , and Ir^{I} THPA complexes could be prepared and successfully applied to the catalytic isomerization of allylic alcohols into carbonyl compounds, as well as in the cycloisomerization of (*Z*)-enynols into furans, in aqueous media.^[7]

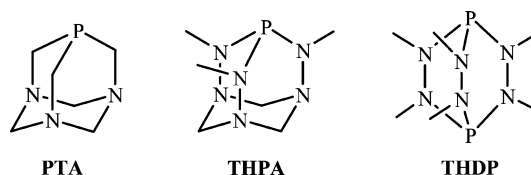


Figure 1. Structure of the cage-like ligands PTA, THPA, and THDP.

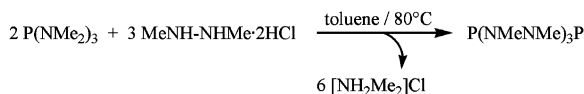
With these precedents in mind, and continuing with our studies aimed at discovering new catalytic systems, we decided to explore the ability of the closely related cage-type ligand tris(1,2-dimethylhydrazino)diphosphane

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$\text{P}(\text{NMeNMe})_3\text{P}$ (THDP; see Figure 1)^[8] to generate water-soluble transition-metal complexes. Remarkably, although this ligand has been known since 1965 and can be easily prepared at multigram-scale by treatment of commercially available tris(dimethylamino)phosphane with 1,2-dimethylhydrazine dihydrochloride (Scheme 1),^[9,10] its coordination chemistry has been scarcely developed. Thus, to the best of our knowledge, the dinuclear compounds $[\{\text{ML}_n\}_2(\mu\text{-THDP})]$ [$\text{ML}_n = \text{W}(\text{CO})_5$,^[11] $\text{Fe}(\text{CO})_4$,^[12] $\text{Ni}(\text{CO})_3$,^[11] AlEt_3 ^[13]] and the mononuclear derivative $[\text{Ni}(\text{CO})_3\{\kappa^1\text{-}(\text{P})\text{-THDP}\}]$ ^[11] are the only THDP-metal complexes reported till now in the literature. In addition, it is also interesting to note that no reports on the involvement of this ligand in homogeneous catalysis have been published.



Scheme 1. Synthesis of the THDP ligand.

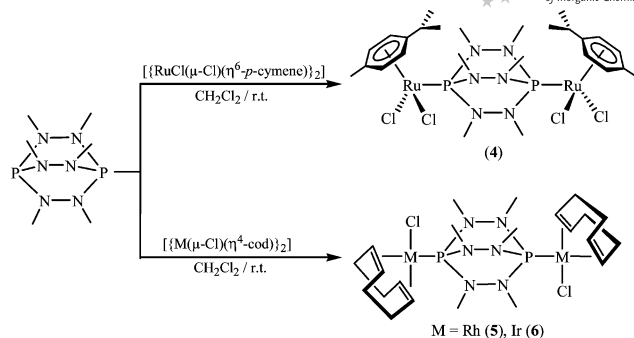
Thus, in the present work we describe the preparation of the first ruthenium, rhodium, and iridium complexes containing the THDP ligand, i.e. $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$, $[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$, and $[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (cod = 1,5-cyclooctadiene), and their successful application to promote the catalytic atom-transfer radical addition of bromotrichloromethane to olefins (Kharasch reaction) in aqueous media.^[14]

Results and Discussion

Synthesis and Characterization of Complexes $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$ (**4**) and $[\{\text{MCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ [$\text{M} = \text{Rh}$ (**5**), Ir (**6**)]

The dimeric ruthenium(II) complex $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2]$ (**1**) readily reacts with one equivalent of $\text{P}(\text{NMeNMe})_3\text{P}$, in dichloromethane at room temperature, to generate the dinuclear derivative $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$ (**4**) in which the cage-like diphosphane is acting as a bridging ligand (Scheme 2). Remarkably, all attempts to generate the mononuclear derivative $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}(\text{P})\text{-THDP}\}]$ failed, the reactions leading to mixtures containing the dinuclear complex **4** and the unreacted diphosphane even when a large excess of THDP (10 equiv.) was used. Similarly, treatment of dichloromethane solutions of $[\{\text{M}(\mu\text{-Cl})(\eta^4\text{-cod})\}_2]$ [$\text{M} = \text{Rh}$ (**2**), Ir (**3**)] with THDP affords selectively the dinuclear species $[\{\text{MCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ [$\text{M} = \text{Rh}$ (**5**), Ir (**6**)] (Scheme 2) irrespective of the molar ratio used (from 1:1 to 1:10).

Complexes **4–6**, isolated as air- and moisture-stable solids in 89–95% yield, have been characterized by means of multinuclear NMR spectroscopy [^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}]$ as well as elemental analyses, all data being fully consistent with the proposed formulations (details are given in the Exp. Sect.). In particular, their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show the presence of only one signal indicative that both phosphorus nuclei of THDP are in equivalent environments.



Scheme 2. Synthesis of the dinuclear THDP-based complexes **4–6**.

While for complexes **4** and **6** this resonance appears as a simple singlet ($\delta_{\text{P}} = 120.9$ and 98.9 ppm, respectively), for the rhodium complex **5** a more complicated pattern is observed (Figure 2). The spectrum shown in Figure 2 corresponds to the AA' part of a AA'XX' spin system due to $^{103}\text{Rh}\text{--}^{31}\text{P}$ couplings.^[15] As previously observed in related $[\{\text{ML}_n\}_2(\mu\text{-THDP})]$ compounds,^[11–13] the *N*-methyl groups of the THDP ligand resonate in the ^1H NMR spectra as a pseudo-triplet with a $|^3J_{\text{P,H}} + ^4J_{\text{P,H}}|$ separation of 11.6–12.0 Hz. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show also a related pattern for the *N*-Me carbons (ca. $|^2J_{\text{P,C}} + ^3J_{\text{P,C}}| = 8.0$ Hz). As expected for their symmetric structure, only one set of resonances for the *p*-cymene (**4**) and 1,5-cyclooctadiene (**5–6**) ligands is observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (see the Exp. Sect.).

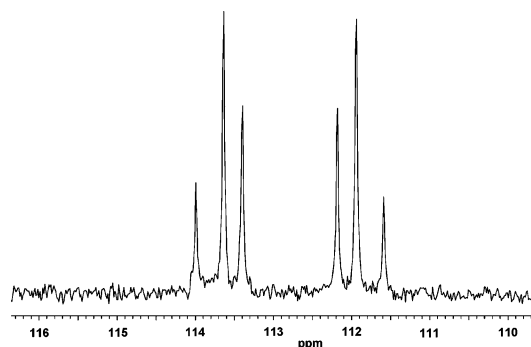


Figure 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.5 MHz, CDCl_3 , 18°C) of complex $[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (**5**).

The structure of the ruthenium(II) complex $[\{\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$ (**4**) has been unambiguously confirmed by means of a single-crystal X-ray diffraction study. An ORTEP view is shown in Figure 3; selected bond lengths and angles are listed in the caption. We note that this compound represents the first example of a THDP complex structurally characterized in the solid-state by X-ray analysis.^[10] It crystallizes in the orthorhombic space group *Pben*, half of the molecule in the asymmetric unit being generated by symmetry. Each nitrogen atom is disordered over two sites, namely N1/N11, N2/N12, and N3/N13, with an occupancy of 80:20, respectively (representation and data given in Figure 3 correspond to the major occupancy).^[16] An usual pseudooctahedral three-legged piano-stool geometry around the metal is observed with

values of the interligand angles P(1)–Ru(1)–Cl(1), P(1)–Ru(1)–Cl(2), and Cl(1)–Ru(1)–Cl(2), and those between the centroid of the arene ring C* and the legs, typical of a pseudo-octahedron. The Ru(1)–P(1) bond length of 2.3173(10) Å compares well with those previously reported for the related cage-like aminophosphane complexes [RuCl₂(η⁶-*p*-cymene)(PTA)] [Ru–P 2.296(2) Å]^[17] and [RuCl₂(η⁶-*p*-cymene)(THPA)] [Ru–P 2.294(2) Å].^[7] It is also interesting to note that, when compared to the X-ray structure of the free ligand,^[10] the coordination of THDP to ruthenium does not alter significantly its geometry, the intra-ligand bond lengths (±0.05 Å) and angles (±10°) remaining almost unchanged.

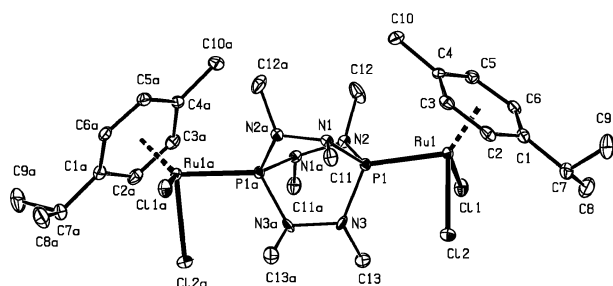


Figure 3. ORTEP-type view of the structure of [{RuCl₂(η⁶-*p*-cymene)}₂(μ-THDP)] (**4**) showing the crystallographic labeling scheme. Atoms labeled with an “a” are related to those indicated by a crystallographic twofold symmetry axis. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths [Å] and angles [°]: Ru(1)–P(1) 2.3173(10), Ru(1)–Cl(1) 2.4043(12), Ru(1)–Cl(2) 2.4157(12), Ru(1)–C* 1.721(1), P(1)–N(1) 1.681(4), P(1)–N(2) 1.663(4), P(1)–N(3) 1.712(5), N(1)–C(11) 1.476(6), N(2)–C(12) 1.469(7), N(3)–C(13) 1.453(6), N(1)–N(2a) 1.440(6), N(3)–N(3a) 1.458(8), C*–Ru(1)–P(1) 133.00(2), C*–Ru(1)–Cl(1) 125.03(1), C*–Ru(1)–Cl(2) 122.78(3), Cl(1)–Ru(1)–Cl(2) 90.29(4), Cl(1)–Ru(1)–P(1) 84.86(4), Cl(2)–Ru(1)–P(1) 87.75(4), Ru(1)–P(1)–N(1) 114.33(15), Ru(1)–P(1)–N(2) 117.48(16), Ru(1)–P(1)–N(3) 119.60(14), N(1)–P(1)–N(2) 103.3(2), N(1)–P(1)–N(3) 98.9(2), N(2)–P(1)–N(3) 100.3(2), P(1)–N(1)–N(2a) 114.3(3), P(1)–N(2)–N(1a) 116.1(3), P(1)–N(3)–N(3a) 114.63(16), P(1)–N(1)–C(11) 119.5(3), P(1)–N(2)–C(12) 124.2(4), P(1)–N(3)–C(13) 121.8(3). C* = centroid of the *p*-cymene ring [C(1), C(2), C(3), C(4), C(5), C(6)].

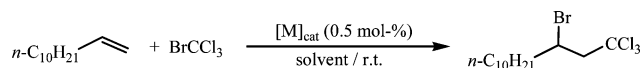
Concerning the solubility of the dinuclear complexes **4**–**6**, it should be noted that they are only sparingly soluble in chlorinated solvents (CH₂Cl₂ and CHCl₃), acetonitrile and tetrahydrofuran, being completely insoluble in alcohols and water. Nevertheless, as discussed in the following section, despite their insolubility in water they could be successfully applied to the catalytic Kharasch-type addition of bromotrichloromethane to olefins in water.

Catalytic Activity of Complexes [{RuCl₂(η⁶-*p*-cymene)}₂(μ-THDP)] (**4**) and [MCl(η⁴-cod)]₂(μ-THDP)] [M = Rh (**5**), Ir (**6**)] in Atom-Transfer Radical Addition Processes

The atom-transfer radical addition (ATRA) of polyhalogenated alkanes across a carbon–carbon double bond, introduced for the first time by Kharasch and co-workers,^[18] constitutes an effective method for the generation of C–C and C–halogen bonds in a single operation.^[14] In the early

years, organic peroxides and related radical initiators were commonly used to promote such a process.^[18] However, the discovery that transition-metal complexes can efficiently catalyze this transformation has increased the scope of its synthetic applications, since they are able to completely suppress the oligomerization and telomerization side reactions usually observed when classical radical initiators are employed.^[14] In particular, among the different metal catalysts reported to date, those based on copper,^[19] nickel,^[14b,20] and specially ruthenium^[14c,14d,21] have provided the best performance in terms of both selectivity and activity. It is also interesting to note that, despite the great interest in this catalytic transformation in synthesis, efforts devoted to developing this reaction in water have been scarce.^[22–24] Thus, to the best of our knowledge, only the palladium-based catalytic system [PdCl₂(NCPh)₂]/dppf [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene] has been applied in a pure aqueous media, promoting efficiently the Kharasch addition of BrCCl₃ or *n*-C₆F₁₃I to several olefins under mild conditions (room temp.).^[22]

With all these precedents in mind we decided to explore the ability of complexes [{RuCl₂(η⁶-*p*-cymene)}₂(μ-THDP)] (**4**) and [MCl(η⁴-cod)]₂(μ-THDP)] (M = Rh (**5**), Ir (**6**)) to act as catalysts for the Kharasch reaction in aqueous media. The addition of bromotrichloromethane to 1-dodecene, to afford 3-bromo-1,1,1-trichlorotridecane, was used as a model reaction (Scheme 3).



Scheme 3. The catalytic Kharasch addition of BrCCl₃ to 1-dodecene.

Firstly, in order to determine the influence of the solvent, we explored the catalytic activity of the dinuclear ruthenium(II) derivative [{RuCl₂(η⁶-*p*-cymene)}₂(μ-THDP)] (**4**) in water, methanol, acetonitrile, dichloromethane, tetrahydrofuran, and toluene. In a typical experiment, 1-dodecene (9 mmol), BrCCl₃ (36 mmol), undecane (1 mmol; used as internal standard), complex **4** (0.045 mmol; 0.5 mol-% with respect to 1-dodecene; 1 mol-% in Ru) and 4 mL of the appropriate solvent were introduced, under an inert atmosphere, into a Schlenk tube and the mixture stirred at room temperature for 3 h. Results are collected in Table 1.

As clearly shown in Table 1, the efficiency shown by complex **4** is strongly dependent on the nature of the solvent employed, the best results being obtained when polar and protic solvents are used, i.e. water and methanol (66 and 62% yield, respectively; entries 1 and 2). In general, the use of aprotic solvents, regardless of their polarity (entries 3–6), reduces considerably the catalytic activity of **4** (a similar behavior has been observed in the absence of solvent; entry 7). As expected, in the absence of complex **4** no addition of BrCCl₃ to 1-dodecene takes place (entries 8–9).^[25,26]

Once we had demonstrated that water is the solvent of choice to perform this ATRA reaction efficiently, we also checked the catalytic activity of the dinuclear Group 9 species [MCl(η⁴-cod)]₂(μ-THDP)] [M = Rh (**5**), Ir (**6**)] under

Table 1. Kharasch addition of bromotrichloromethane to 1-dodecene catalyzed by complex **4**: Influence of the solvent.^[a]

$n\text{-C}_{10}\text{H}_{21} + \text{BrCCl}_3 \xrightarrow[\text{solvent / r.t.}]{\textbf{4} (0.5 \text{ mol-}\%)} n\text{-C}_{10}\text{H}_{21}\text{BrCCl}_3$				
Entry	Catalyst	Solvent	Time [h]	Yield ^[b] [%]
1	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4) ^[c]	H ₂ O	3	66
2	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	MeOH	3	62
3	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	MeCN	3	13
4	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	CH ₂ Cl ₂	3	53
5	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	THF	3	19
6	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	toluene	3	34
7 ^[c]	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	–	3	36
8 ^[d]	–	H ₂ O	3	0
9 ^[d]	–	toluene	3	0

[a] All the reactions were performed under N₂ atmosphere at room temperature using 9 mmol of 1-dodecene, 36 mmol of BrCCl₃, 1 mmol of undecane (internal standard), 0.045 mmol of complex **4** and 4 mL of the corresponding solvent. [b] Yield of 3-bromo-1,1,1-trichlorotridecane determined by GC. [c] Reaction performed in the absence of solvent. [d] Reaction performed in the absence of catalyst. [e] cym = *p*-cymene.

aqueous conditions. As shown in Table 2, both complexes are active catalysts, showing higher performances to that of the ruthenium derivative **4** (entries 2–3 vs. entry 1). Thus, after 3 h 3-bromo-1,1,1-trichlorotridecane is selectively formed in 81 and 77% yield, respectively.^[27] Interestingly, the THDP-based complexes **4–6** are all much more efficient than their dimeric precursors $[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-p-cymene})\}_2]$ (**1**) and $[\{\text{M}(\mu\text{-Cl})(\eta^4\text{-cod})\}_2]$ [M = Rh (**2**), Ir (**3**)] showing that the introduction of the THDP ligand into the coordination sphere of the metals plays a crucial role in attaining good conversions (entries 1–3 vs. 4–6). We have also checked that THDP by itself is unable to promote the ad-

Table 2. Kharasch addition of bromotrichloromethane to 1-dodecene in water: Influence of the metal catalyst.^[a]

$n\text{-C}_{10}\text{H}_{21} + \text{BrCCl}_3 \xrightarrow[\text{H}_2\text{O / r.t.}]{\text{Catalyst (0.5 mol-}\%)} n\text{-C}_{10}\text{H}_{21}\text{BrCCl}_3$				
Entry	Catalyst	Time [h]	% Yield ^[b]	
1	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4) ^[c]	3	66	
2	$[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (5)	3	81	
3	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)	3	77	
4	$[\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-cym})\}_2]$ (1)	3	48	
5	$[\{\text{Rh}(\mu\text{-Cl})(\eta^4\text{-cod})\}_2]$ (2)	3	40	
6	$[\{\text{Ir}(\mu\text{-Cl})(\eta^4\text{-cod})\}_2]$ (3)	3	49	
7 ^[c]	P(NMeNMe) ₃ P (THDP)	3	0	
8 ^[d]	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)/SDS	3	67	
9 ^[d]	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)/CTABr	3	55	

[a] All the reactions were performed under N₂ atmosphere at room temperature using 9 mmol of 1-dodecene, 36 mmol of BrCCl₃, 1 mmol of undecane (internal standard), 0.045 mmol of the corresponding metal complex, and 4 mL of water. [b] Yield of 3-bromo-1,1,1-trichlorotridecane determined by GC. [c] Reaction performed using 0.5 mol-% of the THDP ligand in the absence of any metallic source. [d] 4 mL of a 0.05 M solution of the appropriate surfactant in water was used as solvent. [e] cym = *p*-cymene.

dition of BrCCl₃ to 1-dodecene (entry 7) confirming that metallic species are in all cases the real catalysts.

It is important to note that, under the reaction conditions employed, complexes **4–6** are at first glance not soluble neither in the aqueous phase nor in the organic phase formed by the polyhalogenated alkane and the olefin, the reaction media being apparently heterogeneous.^[28] In light of the possibilities offered by surfactants to perform catalytic organic reactions in water, facilitating the solubility of both the metal catalyst and the substrates,^[29] we decided to explore the Kharasch addition of BrCCl₃ to 1-dodecene in aqueous micelles using the iridium complex $[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (**6**) as a model. The commercially available cetyltrimethylammonium bromide (CTABr) and sodium dodecyl sulfate (SDS) were used as surfactants, the homogeneous reactions being performed in aqueous 0.05 M solutions of each.^[30] As shown in Table 2 (entries 8 and 9), both surfactants have a negative effect on the catalytic activity of complex **6**, leading to the expected product in only 55–67% yield after 3 h (vs. 77% yield without a surfactant; entry 3).

It is known that the catalytic activity of metal complexes in Kharasch-type additions can be increased by adding bases as additives.^[19a,22,31] Thus, in order to improve the activity of complexes **4–6**, some experiments have been performed in the presence of diethylamine, triethylamine, and pyridine. Once again, the aqueous addition of BrCCl₃ to 1-dodecene was used as a model reaction employing 0.5 mol-% of complexes **4–6** and 0.5 equiv. of the amine (both of them with respect to the olefin). As shown in Table 3, in

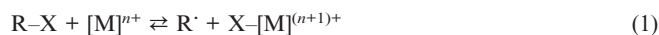
Table 3. Kharasch addition of bromotrichloromethane to 1-dodecene in water: Influence of the additives on the catalytic activity of complexes **4–6**.^[a]

$n\text{-C}_{10}\text{H}_{21} + \text{BrCCl}_3 \xrightarrow[\text{H}_2\text{O / r.t.}]{\textbf{4-6} (0.5 \text{ mol-}\%) \text{ additive (50 mol-}\%)} n\text{-C}_{10}\text{H}_{21}\text{BrCCl}_3$				
Entry	Catalyst	Additive	Time [h]	% Yield ^[b]
1	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4) ^[c]	–	3	66
			7	83
2	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	Et ₂ NH	3	58
3	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	Et ₃ N	3	57
4	$[\{\text{RuCl}_2(\eta^6\text{-cym})\}_2(\mu\text{-THDP})]$ (4)	pyridine	3	0
5	$[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (5)	–	3	81
6	$[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (5)	Et ₂ NH	3	80
7	$[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (5)	Et ₃ N	3	89
			7	93
8	$[\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (5)	pyridine	3	49
9	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)	–	3	77
10	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)	Et ₂ NH	3	90
			7	95
11	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)	Et ₃ N	3	78
12	$[\{\text{IrCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})]$ (6)	pyridine	3	40

[a] All the reactions were performed under N₂ atmosphere at room temperature using 9 mmol of 1-dodecene, 36 mmol of BrCCl₃, 1 mmol of undecane (internal standard), 0.045 mmol of the corresponding metal complex, 4 mL of water, and 4.5 mmol of the additive when appropriate. [b] Yield of 3-bromo-1,1,1-trichlorotridecane determined by GC. [c] cym = *p*-cymene.

the case of the ruthenium catalyst **4** none of the additives allowed us to improve its efficiency, the attained yields being in all cases lower to that obtained in the absence of additive (entries 2–4 vs. entry 1).^[32a] In contrast, for the rhodium **5** and iridium **6** derivatives improvement in the catalytic activity was observed by using Et₃N and Et₂NH, respectively (entry 7 vs. entry 5 and entry 10 vs. entry 9).^[32b] Thus, under these optimized conditions 3-bromo-1,1,1-trichlorotridecane can be generated in 93 (using **5**/Et₃N) and 95% (using **6**/Et₂NH) yield after stirring the heterogeneous mixture for 7 h at room temperature (83% yield can be attained with the ruthenium catalyst **4** after 7 h).

It is commonly accepted that the key step in the Kharasch reaction is the pseudo-oxidative addition of the haloalkane onto the metal complex [Equation (1)].^[14] Therefore, we could argue that the benefic effect of the amines in the case of Rh^I and Ir^I could be associated with the elimination of traces of HX (X = Cl, Br), presumably generated during the radical process, which could give rise to catalytically inactive Rh^{III} and Ir^{III} species via competitive oxidative addition. We note that the catalytic activity of complexes **4–6** is completely suppressed in the presence of the radical scavenger BHT (2,6-di-*tert*-4-methoxyphenol), confirming the involvement of free radicals in the catalytic cycle.



The aqueous Kharasch addition of bromotrichloromethane to other olefinic substrates (1-octene, cyclooctene, 4-penten-2-ol, and styrene) using the optimized catalytic systems, i.e. the Ru^{II} complex **4** by itself, the Rh^I complex **5** associated with Et₃N, and the Ir^I derivative **6** associated with Et₂NH, has also been explored. Selected results are collected in Table 4. In general, the rhodium- and iridium-based systems were found to be much more efficient and versatile than the ruthenium one, which showed a good performance only when 1-octene was used as the substrate, leading to 3-bromo-1,1,1-trichlorononane in 84% yield after 6 h (entry 1). For this particular olefin, the best results were obtained using the rhodium derivative **5** (92% yield after 6 h). This catalyst, along with the Ir^I complex **6**, was also highly efficient for the radical addition of BrCCl₃ to cyclooctene and the functionalized olefin 4-penten-2-ol generating 1-bromo-2-(trichloromethyl)cyclooctane and 4-bromo-6,6,6-trichlorohexan-2-ol, respectively in more than 88% yield after 20–24 h (entries 5–6 and 8–9). Under similar reaction conditions very low yields (6–11%) were attained using **4** (entries 4 and 7). The addition of BrCCl₃ across the C=C bond of cyclooctene and 4-penten-2-ol generates products that contain two stereogenic centers (see Figure 4), the formation of mixtures of two diastereoisomers being in all cases observed. Interestingly, the three catalytic systems employed (based on Ru^{II}, Rh^I, and Ir^I) lead to the same selectivity, i.e. *cis/trans* ratio = 46:54 for cyclooctene and 60:40 for 4-penten-2-ol, suggesting that the stereochemistry-controlling step does not occur in the coordination sphere of the metal. Finally, in the case of styrene (entries 10–12), good results were exclusively obtained using

the rhodium derivative [{RhCl(η⁴-cod)}₂(μ-THDP)] (**5**) albeit a longer reaction time is required (88% yield after 44 h; entry 11).^[33]

Table 4. Catalytic Kharasch addition of bromotrichloromethane to several olefins in water.^[a]

Entry	Olefin	Catalyst	Time [h]	% Yield ^[b]
1	1-octene	4	6	84
2	1-octene	5 /Et ₃ N	6	92
3	1-octene	6 /Et ₂ NH	6	71
4	cyclooctene	4	24	6 (46:54)
5	cyclooctene	5 /Et ₃ N	24	90 (46:54)
6	cyclooctene	6 /Et ₂ NH	24	88 (46:54)
7	4-penten-2-ol	4	20	11 (60:40)
8	4-penten-2-ol	5 /Et ₃ N	20	91 (60:40)
9	4-penten-2-ol	6 /Et ₂ NH	20	92 (60:40)
10	styrene	4	44	0
11	styrene	5 /Et ₃ N	44	88
12	styrene	6 /Et ₂ NH	44	53

[a] All the reactions were performed under N₂ atmosphere at room temperature using 9 mmol of the appropriate olefin, 36 mmol of BrCCl₃, 1 mmol of undecane (internal standard), 0.045 mmol of the corresponding metal complex, 4 mL of water, and 4.5 mmol of the additive when appropriate. [b] Yields determined by GC (diastereomeric ratios are given in brackets).

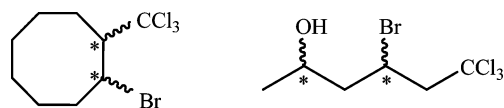
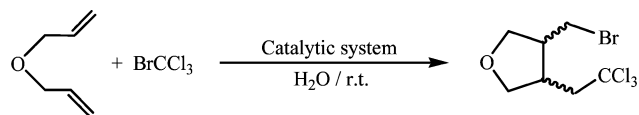


Figure 4. Structure of the products generated from cyclooctene and 4-penten-2-ol.

It is well-known that Kharasch addition of polyhalogenated alkanes to 1,6-diolefins leads usually to cyclization products.^[22,23,34] In accord with this, treatment of diallyl ether with BrCCl₃, in water and in the presence of our optimized catalytic systems, leads in all cases to the selective formation of 3-(bromomethyl)-4-(2,2,2-trichloroethyl)tetrahydrofuran (Scheme 4). Once again, the best results were obtained using the rhodium catalyst **5** which cleanly affords the tetrahydrofuran, as a mixture of diastereoisomers (ratio ca. 85:15), in 74% yield after only 3 h. We note also that, as previously observed with cyclooctene and 4-penten-2-ol, the diastereoselectivity of the process is not dependent on the metallic fragment employed.



Catalytic system	Time	Yield (%)
4 (0.5 mol-%)	20 h	19 (<i>cis</i> / <i>trans</i> ratio = 85:15)
5 (0.5 mol-%) / Et ₃ N (50 mol-%)	3 h	74 (<i>cis</i> / <i>trans</i> ratio = 85:15)
6 (0.5 mol-%) / Et ₂ NH (50 mol-%)	22 h	70 (<i>cis</i> / <i>trans</i> ratio = 85:15)

Scheme 4. Catalytic Kharasch addition of BrCCl₃ to diallyl ether.

Conclusions

In summary, the first ruthenium, rhodium, and iridium complexes containing the cage-type ligand tris(1,2-dimethylhydrazino)diphosphane, namely [{RuCl₂(η⁶-*p*-cymene)}₂-

(μ -THDP)] (**4**) and [$\{MCl(\eta^4\text{-cod})\}_2(\mu\text{-THDP})$] [$M = \text{Rh}$ (**5**), Ir (**6**)], have been synthesized. Despite their insolubility in water, all these species have been found to be active catalysts for the atom-transfer radical addition of bromotrichloromethane to olefins (Kharasch reaction) in aqueous media. Among the THDP-based complexes employed, the rhodium derivative [$\{\text{RhCl}(\eta^4\text{-cod})\}_2(\mu\text{-THDP})$] (**5**) associated with triethylamine was found to be the most active and versatile, representing a rare example of an efficient rhodium catalyst for the Kharasch reaction.^[35]

Experimental Section

General: The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Organic solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers with the exception of compounds $\text{P}(\text{NMeNMe})_3$,^[9] [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-p-cymene})\}_2$] (**1**),^[36] [$\{M(\mu\text{-Cl})(\eta^4\text{-cod})\}_2$] [$M = \text{Rh}$ (**2**),^[37] Ir (**3**)^[38]], [$\text{RuCl}_2(\eta^6\text{-p-cymene})(\text{PTA})$]^[17], and [$\text{RuCl}_2(\eta^6\text{-p-cymene})(\text{THPA})$]^[7] which were prepared by following the method reported in the literature. The C, H, N elemental analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Infrared spectra were recorded with a Perkin–Elmer 1720-XFT spectrometer. NMR spectra were performed with a Bruker DPX300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe_4 or 85% H_3PO_4 as standards. Distortionless enhancement by polarization transfer (DEPT) experiments were carried out for all the compounds reported in this paper. GC and GC/MSD measurements were made with the Hewlett–Packard HP6890 (Supelco Beta-DexTM 120 column; 30 m, 250 μm) system and an Agilent 6890N gas chromatograph coupled to a 5973 mass detector (HP-1MS column; 30 m, 250 μm), respectively.

Synthesis of Complex [$\{\text{RuCl}_2(\eta^6\text{-p-cymene})\}_2(\mu\text{-THDP})$] (4**):** A solution of [$\{\text{RuCl}(\mu\text{-Cl})(\eta^6\text{-p-cymene})\}_2$] (**1**) (0.184 g, 0.300 mmol) and $\text{P}(\text{NMeNMe})_3$ (0.085 g, 0.360 mmol) in dichloromethane (20 mL) was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure to give an orange solid residue, which was washed twice with a hexane/diethyl ether mixture (20 mL, 1:1) and dried in vacuo. Yield 0.239 g (94%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 120.9$ (s) ppm. ^1H NMR (CDCl_3): $\delta = 1.40$ [d, $^3J_{\text{H,H}} = 6.9$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$], 2.29 (s, 6 H, CH_3), 3.00 (virtual t, [$^3J_{\text{P,H}} + ^4J_{\text{P,H}}$] = 11.6 Hz, 18 H, NCH_3), 3.07 [sept, $^3J_{\text{H,H}} = 6.9$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$], 5.29 and 5.62 (br., 4 H each, CH of cymene) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 17.5$ (s, CH_3), 22.4 [s, $\text{CH}(\text{CH}_3)_2$], 30.7 [s, $\text{CH}(\text{CH}_3)_2$], 37.5 (br., NCH_3), 88.1 and 91.1 (s, CH of cymene), 100.2 and 112.5 (s, C of cymene) ppm. $\text{C}_{26}\text{H}_{46}\text{Cl}_4\text{N}_6\text{P}_2\text{Ru}_2$ (848.60): calcd. C 36.80, H 5.46, N 9.90; found C 36.98, H 5.31, N 9.79.

Synthesis of Complexes [$\{MCl(\eta^4\text{-cod})\}_2(\mu\text{-THDP})$] [$M = \text{Rh}$ (5**), Ir (**6**)]:** A solution of the appropriate dimer [$\{M(\mu\text{-Cl})(\eta^4\text{-cod})\}_2$] (**2–3**) (0.400 mmol) and $\text{P}(\text{NMeNMe})_3$ (0.109 g, 0.460 mmol) in dichloromethane (20 mL) was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure to give a yellow solid residue, which was washed twice with a hexane/diethyl ether mixture (20 mL, 1:1) and dried in vacuo.

5: Yield 0.277 g (95%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 112.8$ (AA' part of a AA'XX' spin system) ppm. ^1H NMR (CDCl_3): $\delta = 2.07$ – 2.45 (m, 16 H, CH_2), 3.01 (virtual t, [$^3J_{\text{P,H}} + ^4J_{\text{P,H}}$] = 12.0 Hz, 18 H, NCH_3), 3.91 and 5.60 (br., 4 H each, =CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 28.2$ and 33.3 (s, CH_2), 38.6 (virtual t, [$^2J_{\text{P,C}} + ^3J_{\text{P,C}}$]

= 8.0 Hz, NCH_3), 70.4 and 109.5 (br., =CH) ppm. $\text{C}_{22}\text{H}_{42}\text{Cl}_2\text{N}_6\text{P}_2\text{Rh}_2$ (729.29): calcd. C 36.23, H 5.80, N 11.52; found C 36.33, H 5.90, N 11.41.

6: Yield 0.323 g (89%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 98.9$ (s) ppm. ^1H NMR (CDCl_3): $\delta = 1.78$ – 2.77 (m, 16 H, CH_2), 3.01 (virtual t, [$^3J_{\text{P,H}} + ^4J_{\text{P,H}}$] = 12.0 Hz, 18 H, NCH_3), 3.46 and 5.34 (br., 4 H each, =CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 28.7$ and 34.0 (s, CH_2), 38.8 (virtual t, [$^2J_{\text{P,C}} + ^3J_{\text{P,C}}$] = 8.0 Hz, NCH_3), 53.4 and 100.7 (s, =CH) ppm. $\text{C}_{22}\text{H}_{42}\text{Cl}_2\text{Ir}_2\text{N}_6\text{P}_2$ (907.91): calcd. C 29.10, H 4.66, N 9.26; found C 29.28, H 4.54, N 9.12.

General Procedure for the Catalytic Kharasch Reactions: All the solvents and reactants used in the catalytic processes were employed freshly distilled and deoxygenated. The catalyst precursor (0.045 mmol of dinuclear species or 0.090 mmol of mononuclear complexes), the olefin (9 mmol), bromotrichloromethane (36 mmol), undecane (1 mmol), the appropriate solvent (4 mL) and, when indicated, the additive (4.5 mmol of Et_3N , Et_2NH , or pyridine) were introduced at room temperature into a Schlenk tube. The mixture was then stirred at room temperature for the indicated time, the course of the reaction being monitored by regular sampling and GC or GC/MSD analysis. All the yield values given in the tables are the average of two runs. In all cases, differences between the two measures were within $\pm 3\%$. The identity of the resulting product, which can be isolated in pure form after extraction with CH_2Cl_2 and subsequent purification by column chromatography over silica gel (using hexane/diethyl ether mixtures), was confirmed by comparison of their NMR spectroscopic data with those reported in the literature, i.e. 3-bromo-1,1,1-trichlorotridecane,^[39] 3-bromo-1,1,1-trichlorononane,^[40] 1-bromo-2-(trichloromethyl)cyclooctane,^[41] (1-bromo-3,3,3-trichloropropyl)benzene^[42], and 3-(bromomethyl)-4-(2,2,2-trichloroethyl)tetrahydrofuran.^[34c] with the exception of the unknown compound 4-bromo-6,6,6-trichlorohexan-2-ol which was fully characterized. This compound was isolated as a white solid in 86% yield (using the iridium-based catalytic system), its analytical and spectroscopic data being as follows: $\text{C}_6\text{H}_{10}\text{BrCl}_3\text{O}$ (284.41): calcd. C 25.34, H 3.54; found C 25.49, H 3.61. IR (Nujol): $\tilde{\nu} = 3337$ (ν_{OH}) cm^{-1} . NMR spectroscopic data for the major diastereoisomer: ^1H NMR (CDCl_3): $\delta = 1.22$ (d, $^3J_{\text{H,H}} = 6.4$ Hz, 3 H, Me), 1.90 and 2.12 (m, 1 H each, CH_2CHOH), 3.21 (part A of an AB system of d, $^2J_{\text{H,H}} = 15.7$, $^3J_{\text{H,H}} = 5.2$ Hz, 1 H, CH_2CCl_3), 3.46 (part B of an AB system of d, $^2J_{\text{H,H}} = 15.7$, $^3J_{\text{H,H}} = 5.4$ Hz, 1 H, CH_2CCl_3), 4.06 (m, 1 H, CHOH), 4.54 (m, 1 H, CHBr) ppm. OH signal not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 23.8$ (s, Me), 46.5 (s, CHBr), 48.3 (s, CH_2CHBr), 62.8 (s, CH_2CCl_3), 65.3 (s, CHOH), 97.0 (s, CCl_3) ppm. NMR spectroscopic data for the minor diastereoisomer: ^1H NMR (CDCl_3): $\delta = 1.08$ (d, $^3J_{\text{H,H}} = 6.4$ Hz, 3 H, Me), 2.08 and 2.17 (m, 1 H each, CH_2CHOH), 3.29 (part A of an AB system of d, $^2J_{\text{H,H}} = 16.0$, $^3J_{\text{H,H}} = 4.8$ Hz, 1 H, CH_2CCl_3), 3.41 (part B of an AB system of d, $^2J_{\text{H,H}} = 16.0$, $^3J_{\text{H,H}} = 5.6$ Hz, 1 H, CH_2CCl_3), 4.06 (m, 1 H, CHOH), 4.28 (m, 1 H, CHBr) ppm. OH signal not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 22.7$ (s, Me), 45.2 (s, CHBr), 48.1 (s, CH_2CHBr), 62.4 (s, CH_2CCl_3), 66.0 (s, CHOH), 97.1 (s, CCl_3) ppm.

Catalytic Reactions in the Presence of Surfactants: These catalytic reactions were carried out following a similar procedure replacing the solvent by a 0.05 M aqueous solution (4 mL) of sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTABr).

X-ray Crystal Structure Determination of Complex 4: Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into saturated solutions of complex **4** in dichloromethane. The most relevant crystal and refinement data are collected in

Table 5. Intensity data were collected at low temperature with an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo- K_{α} radiation source ($\lambda = 0.71073 \text{ \AA}$) and equipped with an Oxford Cryosystems Cryostream Cooler Device. A total of 34866 reflections were collected of which 5326 were independent. Multiscan absorption corrections were applied ($T_{\text{min-max}} = 0.52\text{--}0.96$).^[43] The structures were solved by direct methods using SIR92,^[44] and refined by full-matrix, least-squares procedures on F using CRYSTALS.^[45] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.^[46] Non-hydrogen atoms were refined anisotropically. The H atoms were refined using a riding model. The crystallographic plots were made with PLATON.^[47]

Table 5. Crystal data and structure refinement details for **4**.

Chemical formula	$\text{Ru}_2\text{C}_{26}\text{H}_{46}\text{N}_6\text{Cl}_4\text{P}_2 \cdot 2\text{CH}_2\text{Cl}_2$
Mol. mass	1018.45
T [K]	180(2)
Wavelength [$\text{\AA}$]	0.71073
Crystal system	orthorhombic
Space group	$Pbcn$
Crystal size [mm]	$0.50 \times 0.25 \times 0.03$
a [$\text{\AA}$]	13.691(3)
b [$\text{\AA}$]	12.247(2)
c [$\text{\AA}$]	23.701(5)
α [°]	90
β [°]	90
γ [°]	90
Z	4
V [$\text{\AA}^3$]	3974.2(14)
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.702
μ [mm^{-1}]	1.409
$F(000)$	2056
θ range [°]	2.82 to 29.08
Index ranges	$-18 \leq h \leq 18$ $-16 \leq k \leq 12$ $-32 \leq l \leq 32$
Completeness to θ_{max}	99.8%
Number of data collected	34866
Number of unique data	5326 ($R_{\text{int}} = 0.072$)
Number parameters/restraints	202/3
Refinement method	Full-matrix least-squares on F
Goodness of fit on F^2	1.1188
R_1 ^[a] [$I > 3\sigma(I)$]	0.0325
wR_2 ^[a] [$I > 3\sigma(I)$]	0.0373
Largest diff. peak and hole [$\text{e}^{-\text{\AA}^{-3}}$]	0.90 and -0.67

$$[a] R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|; wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}.$$

CCDC-659558 (for **4**) contains supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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