

Rhenium and Manganese Complexes Bearing Amino-Bis(phosphinite) Ligands Synthesis, Characterization, and Catalytic Activity in Hydrogenation of Ketones

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Rhenium and manganese complexes bearing amino-bis(phosphinite) ligands: synthesis, characterization and catalytic activity in hydrogenation of ketones.

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Supporting Information Placeholder

ABSTRACT: A series of rhenium and manganese complexes supported by easily accessible and easily tunable amino-bisphosphinite ligands was prepared and characterized by NMR and IR spectroscopies, HR mass-spectrometry, elemental analysis and X-ray diffraction studies. These complexes have been tested in the hydrogenation of ketones. Notably, one of the rhenium complexes, bearing a NH-moiety, proved significantly more active than the rest of the series. The reaction proceeds well at 120 °C, under 50 bar of H_2, in the presence of 0.5 mol% catalyst and 1 mol% of *t*BuOK. Interestingly, activation of the precatalyst could be followed stepwise by NMR and a rhenium-hydride was characterized by X-ray diffraction studies.

INTRODUCTION

For several decades, since the discovery of Wilkinson's catalyst, the design of homogeneous hydrogenation catalysts has been based on transition metals belonging to groups 8-10, typically iron, cobalt, nickel and Precious Group Metals.[1] Comparatively, hydrogenation catalysts based on group 7 transition metals were quite elusive.[2] In the case of manganese, hydrogenation of alkenes, with either molecular dihydrogen or under water gas shift and synthesis gas conditions, was sporadically described until recently.[3] With rhenium, after the early work of Ephritikhine[4] and Caulton,[5] the group of Berke explored the application of a few nitrosyl (poly)-hydride complexes (e.g. complex **I**, Chart 1, as a representative example) for the hydrogenation of olefins and nitriles.[6] The same group also demonstrated that the rhenium analogue (complex **II**, Chart 1) of Shvo's catalyst is active for the reduction of ketones by transfer hydrogenation, using 2-propanol as hydrogen donor.[7] Also, Gusev reported the reduction of acetophenone, by hydrogen transfer, using a PN(H)P nitrosyl rhenium complex (complex **III**, Chart 1).[8]

However, the association of tridentate PNP ligands and rhenium in coordination chemistry is quite rare[8-9] and the catalytic activities of such complexes quite limited to date.[8, 9i-l, 10] On the opposite, the application of PNP-Mn complexes in hydrogenation and related reactions has seen an impressive explosion in catalysis within only a year.[11]

Among the various tridendate ligands developed,[12] aliphatic PN(H)P ligands, also called "MACHO" type ligands,[13] have been demonstrating a broad versatility with a number of non-noble transition metals to promote hydrogenation reactions (Fe,[14] Co,[15] Ni[16], Mn[11, 17]). Yet, one drawback of these ligands is their high price and relatively low modularity or difficulty of synthesis.[18]

Recently, we have described the first example of rhenium-catalyzed hydrogenation of carbonyl derivatives, with a broad scope and high activity.[10a] The catalyst we used (complex **V**, Chart 1) was based on the typical bis(di-isopropylphosphinoethane)amine ligand, and we have shown, with the help of DFT calculations, that the reaction proceeds through heterolytic cleavage of dihydrogen by a metal-ligand cooperative mechanism.[19] Since the development of cooperative strategies in hydrogenation is of high interest to develop efficient catalytic systems,[20] we were looking for easily accessible ligands, with a higher degree of modularity.

With these aims, we turned our attention toward simpler ligands with phosphinite moieties,[21] synthesized in one step from the readily available corresponding alcohols and chlorophosphines. In particular, we have been interested in the application of amino-bisphosphinite ligand (PONOP), initially developed by Stephan.[22] In association with ruthenium (complex **VI**, Chart 1), the hydrogenation of aromatic and aliphatic esters was achieved.[23]

In this contribution, in line with our interest in group 7 catalysts for reduction reactions,[24] we have prepared a series of new rhenium and manganese complexes bearing amino-bisphosphinite ligands. A comparison of the catalytic activity in hydrogenation of carbonyl derivatives was achieved, using catalyst **V** (Chart 1) as benchmark.

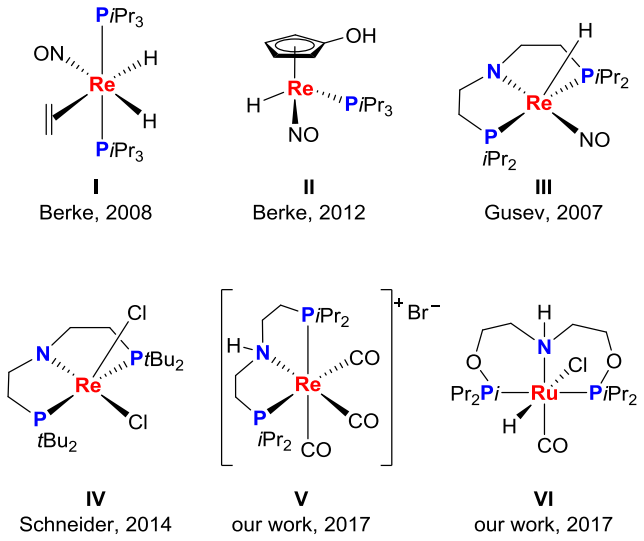


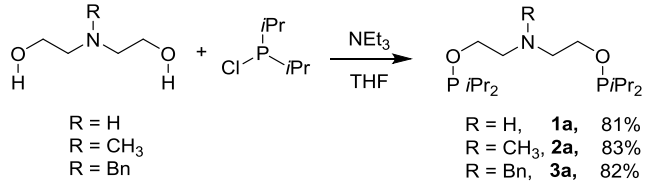
Chart 1. Representative rhenium-based catalysts (I-V) and PNP complexes (III-VI)

RESULTS AND DISCUSSION

Synthesis of rhenium and manganese complexes.

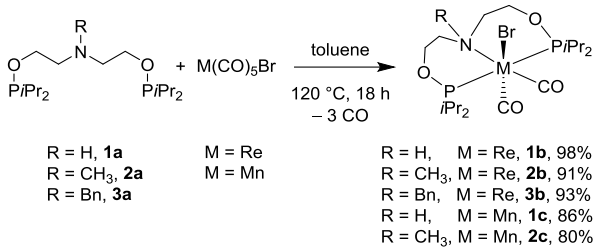
Three bis-aminobis(phosphinite) ligands **1a-3a,** substituted at the nitrogen by H, Me and Bn, respectively, were readily prepared in high yield from the corresponding diethanolamine and chlorodiisopropylphosphine in THF in the presence of Et_3N following literature procedures (Scheme 1).[22]

Scheme 1. Synthesis of PONOP ligands 1a-3a.



Rhenium **1b-3b** and manganese **1c-2c** complexes were synthesized starting from $M(CO)_5Br$ (M = Re/Mn) and the corresponding ligand by heating at toluene reflux overnight (Scheme 2). Rhenium complexes were obtained as off-white solids in excellent yields after one recrystallization step, and manganese ones as orange powders. Note that in the case of ligand **3a** and manganese, a black oily crude product was obtained and could not be purified. All the complexes were fairly stable to air and moisture and could be handled without special precautions; yet they were best stored under argon in the dark at room temperature.

Scheme 2. Synthesis of rhenium (1b-3b) and manganese (1c-2c) complexes.



All the complexes were diamagnetic and were fully characterized by NMR (^1H, ^{13}C and ^{31}P) and IR spectroscopies, HR-mass spectrometry and elemental analysis. Coordination of the tridentate ligand was confirmed by the presence of a single signal in the $^{31}P\{^1H\}$ NMR spectra (for rhenium complexes: δ 128.8, 130.1, and 129.4 ppm for **1b**, **2b**, and **3b** respectively; for manganese complexes: δ 174.7 and 172.2 ppm for **1c** and **2c**, respectively). In contrast with our previous synthesis of complex **V**, and similar PNP and PN^3P-Mn complexes, for which cationic tricarbonyl complexes were obtained alone or as a mixture of neutral and cationic compounds, with this family of PONOP ligands, neutral dicarbonyl complexes were exclusively obtained, as confirmed by elemental analysis.

The molecular solid-state structures of the five complexes were also confirmed by single crystal X-ray diffraction studies. Representative perspective figures are disclosed in Figures 1-5 for **1b**, **2b**, **3b**, **1c** and **2c,** respectively. In all the cases, the metal lies in an octahedral environment, the tridentate ligand being in a meridional coordination mode, and the two carbonyl ligands in *cis*-position. The bromide atom was found randomly in *cis* or *trans* position with respect to the substituent on the nitrogen atom. The meridional coordination of the PONOP ligand contrasts with the facial arrangement observed in complex **V** (Chart 1). This isomer corresponds to the most stable one, compared to the facial one according to DFT calculations performed by us and others.[8, 10a] In line with this geometry, Tisato and Bolzati have found that in the case of $[(PN(H)P)ReCl_3]$ meridional coordination is also preferred.[9e-g, 25]

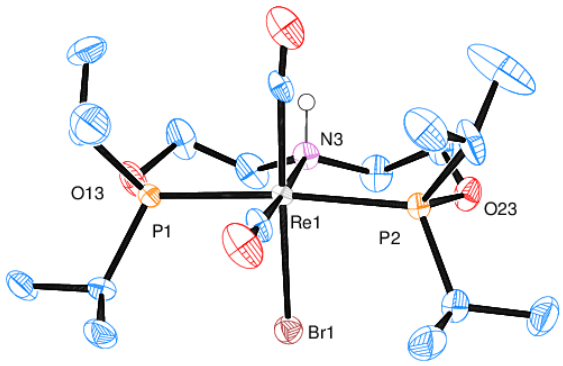


Figure 1. Perspective view of the molecular structure of complex **1b** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms, except N*H*, were omitted for clarity. The bromide atom is disordered over two positions, only one of which is depicted.

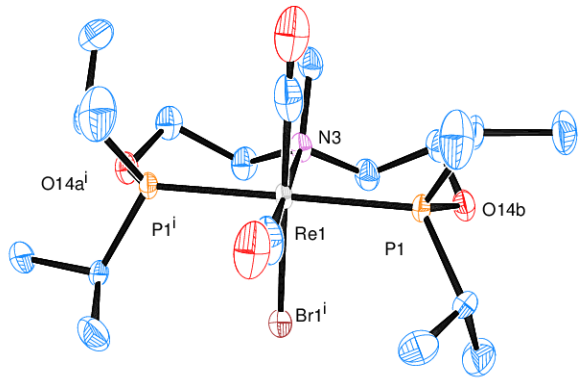


Figure 2. Perspective view of the molecular structure of complex **2b** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms were omitted for clarity. Two configurations of the compound are superimposed in the crystal structure, only one is depicted.

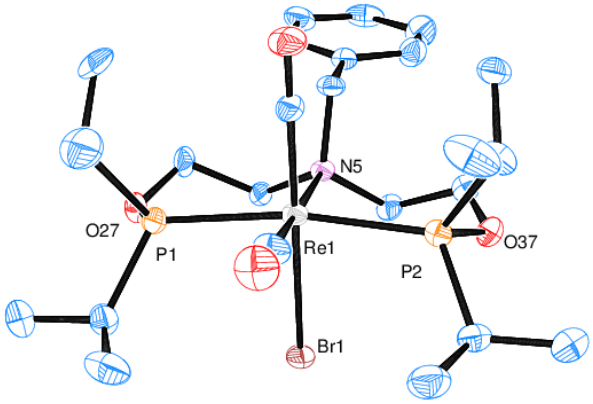


Figure 3. Perspective view of the molecular structure of complex **3b**, with thermal ellipsoids drawn at 50% probability. Hydrogen atoms were omitted for clarity.

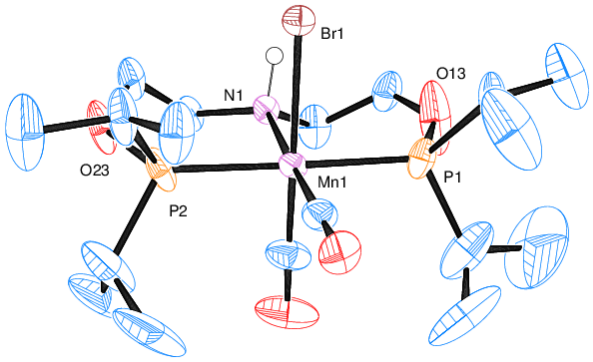


Figure 4. Perspective view of the molecular structure of complex **1c**, with thermal ellipsoids drawn at 50% probability. Hydrogen atoms, except N*H*, were omitted for clarity.

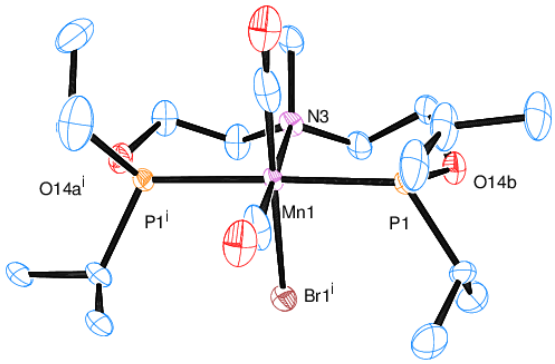


Figure 5. Perspective view of the molecular structure of complex **2c** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms were omitted for clarity. Two configurations of the compound are superimposed in the crystal structure, only one is depicted.

Catalytic Experiments.

With these new complexes in hand, we explored their catalytic activity in the reduction of ketones with molecular hydrogen (Table 1). Based on the optimized conditions defined for the reduction of acetophenone using complex **V**,[23] initial experiments were performed on acetophenone as model substrate at 110 °C, with 1 mol% catalyst and 2 mol% *t*BuOK loadings. Under 30 bar of H_2, (pre)catalyst **1b** bearing a secondary amine led to a promising conversion of 87% after 20 h of reaction. No reaction occurred when the catalysts bear a tertiary amine such as in **2b** and **3b** (entries 2 and 3). This clear difference of reactivity is in line with the importance of *N*H-moieties to promote hydrogenation via the "classical" cooperative ligand-metal mechanism.[19b-e, 20b, 26]

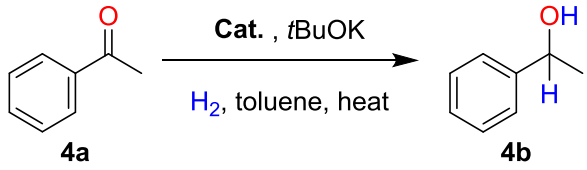
At 110 °C, the influence of the pressure was limited, as increasing to 50 bar or lowering to 10 bar only induced minor variations of the conversion (90 to 81%, entries 4-5). On the other hand, the temperature was more crucial to reach high conversion: from 120 °C to 70 °C, the conversion dropped from 98% to 38% over the 20 h reaction time (entries 6-8).

Interestingly, the catalyst loading could be halved down to 0.5 mol% at 120 °C without apparent degradation of the activity (entry 9 *vs* entry 6), and even lowered to 0.1 mol% (93% conv., entry 10) leading to an overall TON of 930.[27,28]

It is worth noting that, with the simpler PONOP ligand, the same catalytic load of 0.5 mol% can be reached with **1b** as with complex **V** based on PNP ligand, yet at a higher temperature (120 °C *vs* 70 °C, entry 9 *vs* 11).

The manganese complexes were also tested, but were found to be significantly less active: only 25% conversion was obtained with 1 mol% catalyst at 120 °C under 50 bar of hydrogen. Surprisingly, the *N*-Me complex **1c** led to nearly the same conversion as the *N*H one **2c**, which suggests that the reaction with these Mn complexes may proceed via a different mechanism.[20b, 26]

Table 1: Optimization of reaction parameters for the hydrogenation of acetophenone [a]

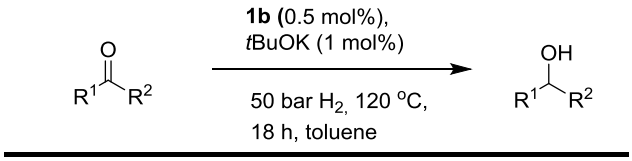


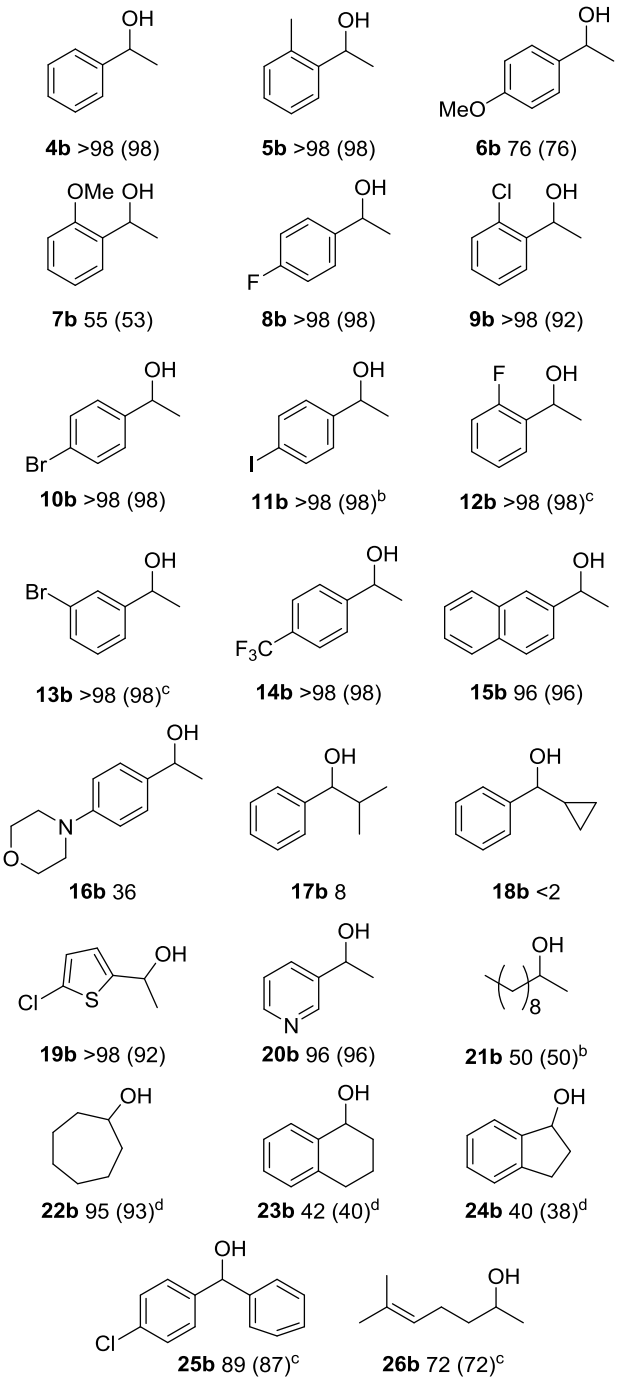
Entry	Cat. (mol%)	H_2 (bar)	*t*BuOK (mol%)	Temp. (°C)	Time (h)	Conv. (%)[b]
1	**1b** (1.0)	30	2.0	110	20	87
2	**2b** (1.0)	30	2.0	110	20	2
3	**3b** (1.0)	30	2.0	110	20	0
4	**1b** (1.0)	50	2.0	110	20	90
5	**1b** (1.0)	10	2.0	110	20	81
6	**1b** (1.0)	50	2.0	120	20	98
7	**1b** (1.0)	50	2.0	100	20	80
8	**1b** (1.0)	50	2.0	70	20	38
9	**1b** (0.5)	50	1.0	120	20	98
10	**1b** (0.1)	50	5.0	120	20	93
11	**V** (0.5)	30	1.0	70	16	98
12	**1c** (1.0)	50	2.0	120	20	25
13	**2c** (1.0)	50	2.0	120	20	20

[a] General conditions: Under argon, an autoclave was charged with the (pre)catalyst, toluene (1.0 mL), followed by acetophenone (0.25 mmol, 29 μL) and *t*BuOK, in this order. The autoclave was then charged with H_2 and heated in an oil bath. [b] The conversion (%) was determined by ^{1}H NMR on the crude reaction mixture.

With the optimized conditions in hand (Table 1, entry 9), we probed the generality of the reaction (Table 2). In general, from regular aromatic ketones (**4a-15a**), the corresponding alcohols (**4b-15b**) were obtained in good to high yields with both electron-donating and electron-withdrawing substituents. The reactivity was noticeably affected by steric hindrance in the α-position to the carbonyl group, as isobutyrophenone and cyclopropylphenylketone (**17a-18a**) were very slowly or not reduced, respectively, under standard conditions. Cyano or nitro group at the *para* position of the aromatic ring also inhibited the reaction. This lack of reactivity might be attributed to the weak, yet competitive coordination abilities toward the catalyst of such functional group. Additionally, heteroaromatic substrates based on thiophene (**19a**) and pyridine (**20a**) were smoothly reduced. Not unexpectedly, aliphatic, cyclic and diaryl ketones (**21a-26a**) required slightly harsher conditions to be hydrogenated. Most interestingly, the reaction is chemoselective towards C=O, as the remote trisubtituted C=C bond was not hydrogenated (**26b**). In the case of benzylideneacetone, as a model of α,β-unsaturated ketones, the starting material was fully converted into a mixture of corresponding unsaturated alcohol (27%) and saturated alcohol (24%) along with the saturated ketone (49%) as the major product.

Table 2. Scope of the hydrogenation of ketones to give alcohols under the catalysis of **1b**[a]





[a] General conditions: Under argon, an autoclave was charged with complex **1b** (0.5 mol%), toluene (2.0 mL), followed by ketone (2 mmol) and *t*BuOK (1.0 mol%), in this order. The autoclave was then charged with H_2 (50 bar). The mixture was stirred for 18 h at 120 °C in an oil bath. The conversion (%) was determined by ^{1}H NMR on the crude reaction mixture. Isolated yields (%) are provided in parentheses. [b] **1b** (1.0 mol%), *t*BuOK (2.0

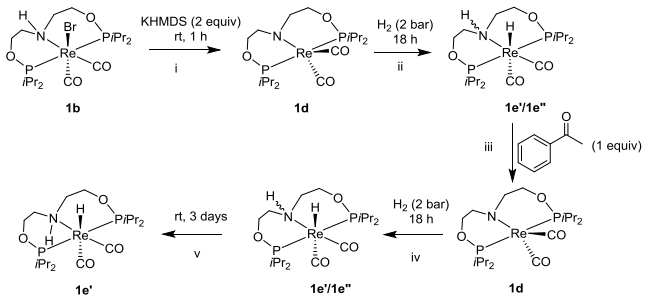
mol%), 130 °C. [c] **1b** (2.0 mol%), *t*BuOK (4.0 mol%), 130 °C. [d] **1b** (2.0 mol%), *t*BuOK (4.0 mol%), 150 °C.

Mechanistic investigations.

In order to get more insights into the operative mechanism of this rhenium-catalyzed hydrogenation, a series of experiments in Young-type NMR tubes was conducted (Scheme 3) and followed by ^{31}P NMR spectroscopy (Figure 6). First, complex **1b** (δ (^{31}P{^{1}H}) = 128.8 ppm) reacted with KHMDS (2.0 equiv.) in toluene-d_8 (the reaction proved more selective with 2 equiv than 1 equiv; see Figure S82, S.I.). The complex was fully converted at room temperature within short time (typically 1 h) into a new species (**1d**) displaying a single singlet at δ 156.1 ppm. The ^{1}H NMR spectrum was consistent with a highly symmetrical species. Even if single crystals of compound **1d** suitable for X-ray diffraction studies could not be obtained, one can reasonably assume that the structure of **1d**, resulting from the deprotonation of **1b** with the base, is likely to be a neutral dicarbonyl complex with an amido-ligand.[9a, 29] Upon addition of H_2 (2 bar) inside the NMR tube, complex **1d** reacted slowly at room temperature overnight (or in 1 h at 120 °C, see Figures S83-S84, S.I.) to afford two rhenium hydride species, **1e'** and **1e"**, in a ratio 2:5, exhibiting typical signals in NMR (**1e'** δ(^{31}P{^{1}H}) = 157.8 ppm, δ(^{1}H) = –2.45 ppm (t, *J* = 25.9 Hz), **1e"** δ(^{31}P{^{1}H}) = 153.5 ppm, δ(^{1}H) = –2.07 ppm (t, *J* = 28.8 Hz)). The two hydride complexes probably correspond to isomers, the Re–H bond being presumably either *syn* or *anti* to the *N*–H one.[10a, 29c, 30]

After releasing the H_2 pressure, acetophenone (1.0 equiv.) was charged in the NMR tube. After 18 h at 120 °C, the signals of **1e'** and **1e"** disappeared, while concomitantly the characteristic signal of **1d** reappeared. In the ^{1}H NMR spectrum, the signal of acetophenone also disappeared. Yet, the formation of 1-phenylethanol, resulting from the transfer of the two protons from **1e** to the ketone, could not be detected, likely as it reacted with excess KHMDS to form an alkoxide salt insoluble in toluene (Note that at the end of the series of reactions, upon addition of H_2O, the characteristic signals of 1-phenylethanol were eventually observed). Finally, rhenium hydride complexes were regenerated by pressurizing again the NMR tube under H_2 and heating. Interestingly, after 3 days, a slow isomerization took place, leading exclusively to **1e'**.

Scheme 3: Stoichiometric reactions



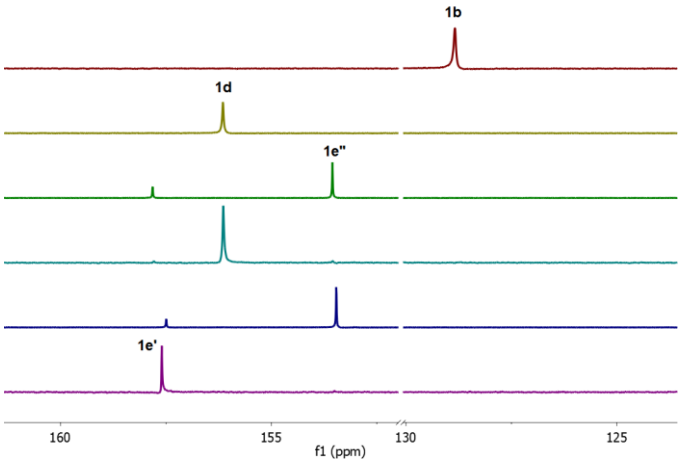


Figure 6. Monitoring of the stoichiometric reactions described on Scheme 3 by ^{31}P{^{1}H} NMR spectroscopy, starting from **1b** (top), to **1e'** (bottom), via the reaction steps *i* to *v*.

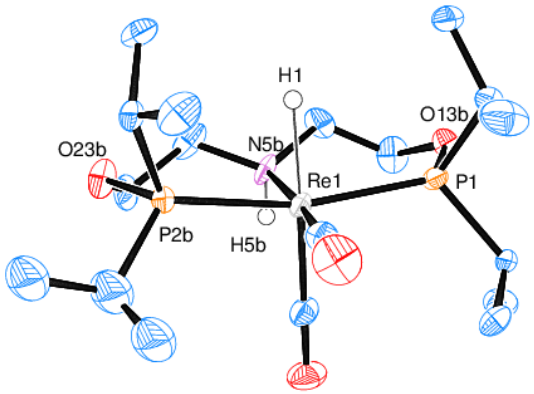


Figure 7. Perspective view of the molecular structure of complex **1e'**, with thermal ellipsoids drawn at 50% probability. Hydrogen atoms, except N*H* and hydride, were omitted for clarity.

Single crystals suitable for X-ray diffraction studies were obtained for the rhenium hydride complex and revealed the Re–H and *N*–H bonds in *anti* position (Figure 7). We assume that this isomer corresponds to the more stable one, and we therefore assigned it as **1e'**. **1e"**, with the two protons in a *syn*-configuration would be the active catalytic species.[10a] The epimerization of the *N*–H bond is likely to occur in the presence of base or traces of alcohol.

Finally, having identified the NMR signature of the rhenium-hydride complexes, the integrity of the catalyst after a catalytic run was also confirmed, by running in an autoclave the hydrogenation of acetophenone with 20 mol% of **1b** (and 40 mol% of *t*BuOK) in toluene-d_8 at 110 °C for 3 h and by

analyzing the crude reaction mixture by NMR; this revealed the sole presence of the two Re–H complexes **1e'** and **1e"** in the $^{31}P\{^{1}H\}$ NMR spectrum (see Figures S80-81).

CONCLUSION

In conclusion, five new complexes based on easily accessible and easily tunable amino-bisphosphinite ligands have been prepared and fully characterized. Rhenium complex **1b**, displaying metal–ligand cooperation, is an efficient catalyst for the hydrogenation of ketones. The reaction proceeds at 120 °C with the same catalyst load as the less affordable amino-bisphosphine rhenium catalyst **V** (chart 1). Interestingly, the reaction could be monitored stepwise by NMR and a rhenium hydride was isolated and crystallized.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon or in an argon-filled glove-box. Toluene, THF, diethyl ether (Et_2O), and CH_2Cl_2 were dried over MBraun MB-SPS-800 solvent purification system and degassed by thaw-freeze cycles. Technical grade pentane and diethyl ether were used for column chromatography. Analytical TLC was performed on Merck $60F_{254}$ silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 µm, 60Å). All reagents were obtained from commercial sources and liquid reagents were dried on molecular sieves and degassed prior to use. Rhenium pentacarbonyl bromide, 98%, and manganese pentacarbonyl bromide, min 98%, were purchased from Strem Chemicals.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, C_6D_6 or toluene-d_8 at ambient temperature unless otherwise stated, on Bruker AVANCE 500, AVANCE 400 and AVANCE 300 spectrometers at 500, 400 and 300 MHz, respectively. ^{1}H and ^{13}C spectra were calibrated using the residual solvent signal as internal standard (^{1}H: $CDCl_3$ 7.26 ppm, CD_2Cl_2 5.32 ppm, C_6D_6 7.16 ppm, toluene-d_8 2.08 ppm, ^{13}C: $CDCl_3$ 77.16 ppm, CD_2Cl_2 53.84 ppm, toluene-d_8 20.43 ppm, C_6D_6 128.06 ppm). IR spectra were measured by Shimadzu IR-Affinity 1 with ATR equipment or in solution. HR–MS spectra and microanalyses were carried out by the corresponding facilities at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest), University of Rennes 1.

X-ray diffraction data were collected on D8 VENTURE Bruker AXS diffractometer equipped with a PHOTON 100 CMOS detector, using multilayers monochromated Mo-Kα radiation (λ = 0.71073 Å) at T = 150 K. X-Ray data are summarized in the Supporting Information.

Ligands **1a**-**3a** were prepared following literature procedures.[22]

Synthesis of complexes

*Complex **1b***. Representative procedure. Bis(2-((diisopropylphosphino)oxy)ethyl)amine **1a** (0.240 mmol, 80.9 mg, 1.0 equiv.) was added to a solution of $Re(CO)_5Br$ (0.240 mmol, 97.5 mg, 1.0 equiv.) in anhydrous toluene (2 mL). The mixture was stirred at 100 °C overnight. Toluene was then evaporated. The crude residue was then recrystallized from dichloromethane (1 mL) and pentane (5 mL) to afford white flake crystals. The white solid was washed with pentane (2×2 mL) to afford pure compound (146.5 mg, 93%). Single crystals suitable for X-Ray diffraction studies were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **1b** at r.t.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.22 – 4.01 (m, 4H, N-CH_2), 3.46 – 3.28 (m, 2H, $CH_{i\mathrm{Pr}}$), 3.23 – 3.09 (m, 2H, O-CH_2), 3.08 – 2.98 (m, 2H, O-CH_2), 2.81 – 2.58 (m, 2H, $CH_{i\mathrm{Pr}}$), 1.40 – 1.13 (m, 24H, $CH_{3i\mathrm{Pr}}$). (Note : the N*H* proton was not observed in the spectrum)

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 128.8.

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 202.0 (br., CO), 197.2 (br., CO), 66.19 (N-CH_2), 58.75 (t, *J* = 3.4 Hz, O-CH_2), 31.76 (t, *J* = 17.9 Hz, $CH_{i\mathrm{Pr}}$), 29.55 (t, *J* = 11.6 Hz, $CH_{i\mathrm{Pr}}$), 18.92 (t, *J* = 2.7 Hz, $CH_{3i\mathrm{Pr}}$), 18.33($CH_{3i\mathrm{Pr}}$), 17.81 (t, *J* = 2.1 Hz, $CH_{3i\mathrm{Pr}}$), 16.43 ($CH_{3i\mathrm{Pr}}$).

Anal. Calc (%). for ($C_{18}H_{37}NO_4BrP_2Re$): C, 32.78; H, 5.65; N, 2.12. Found: C, 32.53; H, 5.60; N, 2.06.

HR MS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{37}NO_4{}^{79}BrNaP_2{}^{187}Re$ 682.0831, found 682.0824 (1 ppm); m/z $[M-.Br]^+$ calcd for $C_{18}H_{37}NO_4P_2{}^{187}Re$ 580.1755, found 580.1749 (0 ppm)

IR (ν, cm^{-1}, CH_2Cl_2): 1929, 1840.

*Complex **2b***. Following the same procedure as for the synthesis of complex **1b**, starting from **2a** (100.0 mg, 0.284 mmol) and $Re(CO)_5Br$ (115.6 mg, 0.284 mmol), complex **2b** was obtained as a white solid (174.6 mg, 92%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.46 – 4.33 (m, 2H, N-CH_2), 4.33 – 4.21 (m, 2H, O-CH_2), 4.14 – 3.97 (m, 2H, N-CH_2), 3.40 – 3.27 (m, 2H, $CH_{i\mathrm{Pr}}$), 3.01 (s, 3H, N-CH_3), 2.87 – 2.72 (m, 2H, $CH_{i\mathrm{Pr}}$), 1.96 (dd, *J* = 13.6, 3.8 Hz, 2H, O-CH_2), 1.39 – 1.14 (m, 24H, $CH_{3i\mathrm{Pr}}$).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 199.8 (br., CO), 198.4 (br. CO), 64.0 (N-CH_2), 63.2 (t, *J* = 3 Hz, O-CH_2), 50.7 (N-CH_3), 32.7 (t, *J* = 13 Hz, $CH_{i\mathrm{Pr}}$), 31.6 (t, *J* = 17 Hz, $CH_{i\mathrm{Pr}}$), 18.5 (t, *J* = 2 Hz, $CH_{3i\mathrm{Pr}}$), 18.2 (t, *J* = 2 Hz, $CH_{3i\mathrm{Pr}}$), 18.0 ($CH_{3i\mathrm{Pr}}$), 17.2 ($CH_{3i\mathrm{Pr}}$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 129.4.

Anal. Calc (%). for ($C_{19}H_{39}NO_4BrP_2Re$): C, 33.88; H, 5.84; N, 2.08, Found: C, 33.84; H, 5.94; N, 2.16.

HR-MS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{39}NO_4{}^{79}BrNaP_2{}^{187}Re$ 696.0993, found 696.0983 (1 ppm); m/z $[M+K]^+$ calcd for $C_{19}H_{39}NO_4{}^{79}BrKP_2{}^{187}Re$ 712.07269, found 712.0714 (2 ppm)

IR (ν, cm^{-1}, CH_2Cl_2): 1925, 1834.

IR (ν, cm^{-1}, ATR): 1911, 1822.

*Complex **3b***. Following the same procedure as for the synthesis of complex **1b**, starting from **3a** (100.0 mg, 0.234 mmol) and $Re(CO)_5Br$ (95.0 mg, 0.234 mmol), complex **3b** was obtained as a white solid (163.6 mg, 93%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43 – 7.27 (m, 3H, H_{Ar}), 7.07-7.02 (m, 2H, H_{Ar}), 4.82 (s, 2H, CH_2-C_6H_6), 4.75 – 4.57 (m, 2H, N-CH_2), 4.21 – 4.01 (m, 2H, N-CH_2), 3.86 (dd, *J* = 13.5, 9.8 Hz, 2H, O-CH_2), 3.40 (dhept, *J* = 14.1, 7.1 Hz, 2H, $CH_{i\mathrm{Pr}}$), 2.96-2.81 (m, 2H, $CH_{i\mathrm{Pr}}$), 2.25 (dd, *J* = 14.3, 4.9 Hz, 2H, O-CH_2), 1.58 – 1.13 (m, 24H, $CH_{3i\mathrm{Pr}}$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 131.0.

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 199.6 (br. t, *J* = 7 Hz, CO), 198.7 (br. t, *J* = 7 Hz, CO), 132.1 (C_{Ar}), 129.09 (C_{Ar}), 129.06 (C_{Ar}), 64.0(N-CH_2), 61.4 (CH_2-C_6H_6), 56.1 (t, *J* = 2 Hz, O-CH_2), 33.0 (t, *J* = 12 Hz, $CH_{i\mathrm{Pr}}$), 31.7 (t, *J* = 17 Hz, $CH_{i\mathrm{Pr}}$), 18.7 (t, *J* = 2 Hz, $CH_{3i\mathrm{Pr}}$), 18.11 ($CH_{3i\mathrm{Pr}}$), 18.06 (t, *J* = 2 Hz, $CH_{3i\mathrm{Pr}}$), 17.5 ($CH_{3i\mathrm{Pr}}$).

Anal. Calc (%). for ($C_{25}H_{43}NO_4BrP_2Re$): C, 40.05; H, 5.78; N, 1.87, Found: C, 39.77; H, 5.88; N, 1.87.

HR-MS (ESI): m/z $[M]^{+\cdot}$ calcd for $C_{25}H_{43}NO_4{}^{79}BrP_2{}^{187}Re$ 749.1408, found 749.1391 (2 ppm)

IR (ν, cm^{-1}, CH_2Cl_2): 1925, 1834.

IR (ν, cm^{-1}, ATR): 1932, 1832.

*Complex **1c***. Following the same procedure as for the synthesis of complex **1b**, starting from **1a** (100.0 mg, 0.296 mmol) and $Mn(CO)_5Br$ (81.4 mg, 0.296 mmol), complex **1c** was obtained as an orange solid (129.5 mg, 82%)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.30 – 3.85 (m, 4H, CH_2), 3.66 – 3.32 (m, 2H, $CH_{i\mathrm{Pr}}$), 3.24 – 2.92 (m, 3H, NH+ CH_2), 2.81 (dd, *J* = 10.4, 3.1 Hz, 2H, CH_2), 2.75 – 2.62 (m, 2H, $CH_{i\mathrm{Pr}}$), 1.47 – 1.14 (m, 24H, $CH_{3i\mathrm{Pr}}$).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ 64.8 (CH_2), 57.4 (br., CH_2), 31.4-31.1 (m, 2C, $CH_{i\mathrm{Pr}}$), 18.3 (br., $CH_{3i\mathrm{Pr}}$), 17.9 ($CH_{3i\mathrm{Pr}}$), 17.6 (br., $CH_{3i\mathrm{Pr}}$), 16.5 (br., $CH_{3i\mathrm{Pr}}$). (CO signals not detected)

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ 174.7.

Anal. Calc (%). for ($C_{18}H_{37}NO_4BrP_2Mn$): C, 40.92; H, 7.06; N, 2.65, Found: C, 40.82; H, 6.73; N, 2.42.

HR-MS (ESI): m/z $[M]^{+\cdot}$ calcd for $C_{18}H_{37}NO_4{}^{79}BrP_2Mn$ 527.0756, found 527.0754 (0 ppm); m/z $[M-.2CO]^{+\cdot}$ calcd for $C_{16}H_{37}NO_2{}^{79}BrP_2Mn$ 471.08579, found 471.0854 (1 ppm)

IR (ν, cm^{-1}, CH_2Cl_2): 1953, 1927, 1846.[31]

Complex ***2c.*** Following the same procedure as for the synthesis of complex **1b**, starting from **2a** (100.0 mg, 0.284 mmol) and $Mn(CO)_5Br$ (78.1 mg, 0.284 mmol), complex **2c** was obtained as an orange solid (124.0 mg, 80%).

^1H NMR (400 MHz, CD_2Cl_2) δ 4.41-4.25 (br. s, 2H, CH_2), 4.11 – 3.80 (br., 4H, CH_2), 3.53-3.38 (br., 2H, $CH_{i\mathrm{Pr}}$), 2.91-2.73 (br., 5H, $CH_{i\mathrm{Pr}}$ + N-CH_3), 1.72-1.61 (br., 2H, CH_2), 1.50-1.19 (br. m, 24H, $CH_{3i\mathrm{Pr}}$).

$^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 61.4 (CH_2), 61.3 (CH_2), 46.9 (N-CH_3), 31.5-31.1 (m, 2C, $CH_{i\mathrm{Pr}}$), 17.4 ($CH_{3i\mathrm{Pr}}$), 16.8 ($CH_{3i\mathrm{Pr}}$), 16.5 ($CH_{3i\mathrm{Pr}}$), 16.4 ($CH_{3i\mathrm{Pr}}$). (CO signals not detected)

$^{31}P\{^1H\}$ NMR (162 MHz,CD_2Cl_2) δ 172.2.

Anal. Calc (%). for ($C_{19}H_{39}NO_4BrP_2Mn$).(CH_2Cl_2): C, 38.30; H, 6.59; N, 2.23, Found: C, 38.21; H, 6.48; N, 2.88.

HR-MS (ESI): m/z $[M-Br]^+$ calcd for $C_{19}H_{39}NO_4P_2Mn$ 462.1729, found 462.1737 (2 ppm);m/z $[M]^{+\cdot}$ calcd for $C_{19}H_{39}NO_4{}^{79}BrP_2Mn$ 541.09127, found 541.0912 (0 ppm); m/z $[M-.2CO]^{+\cdot}$ calcd for $C_{17}H_{39}NO_2{}^{79}Br\ P_2Mn$ 485.10144, found 485.1015 (0 ppm)

IR (ν, cm^{-1}, CH_2Cl_2): 1946, 1923, 1842. [29]

NMR scale synthesis of complex ***1d.*** In a Young-type NMR tube, complex **1b** (8.4 mg, 0.012 mmol) was added to a solution of KHMDS (4.8 mg, 0.024 mmol) in dry toluene-d_8 (ca. 0.5 mL) at room temperature. NMR spectra were recorded after 1 h of reaction.

^1H NMR (400 MHz, C_7D_8) δ 3.77-3.68 (br. m, 4H, CH_2), 2.45 (br. s, 4H, CH_2), 2.30 – 2.21 (m, 4H, $CH_{i\mathrm{Pr}}$), 1.25 – 1.11 (m, 24H, $CH_{3i\mathrm{Pr}}$).

$^{31}P\{^1H\}$ NMR (162 MHz C_7D_8) δ 156.1.

$^{13}C\{^1H\}$ (101 MHz, C_7D_8) δ 207.3 (t, *J* = 6.2 Hz, CO), 74.3 (t, *J* = 3.8 Hz, CH_2), 63.9 (t, *J* = 7.8 Hz, CH_2), 31.8 (br s, $CH_{i\mathrm{Pr}}$), 17.1 (br s, $CH_{3i\mathrm{Pr}}$), 16.7 (br s, $CH_{3i\mathrm{Pr}}$).

NMR scale synthesis of complexes ***1e'*** and ***1e".*** The NMR tube containing the solution of **1d** in toluene-d_8, obtained at the previous step, was pressurized with H_2 (2 bar). NMR spectra were recorded after 18 h of reaction at r.t. Single crystals suitable for X-Ray diffraction studies were obtained by slow evaporation in the glovebox.

Complex **1e'.**

^1H NMR (400 MHz, toluene-d_8) δ 3.74 – 3.65 (m, 2H), 3.40 – 3.30 (m, 2H), 2.38-2.29 (m, 2H), 2.20 – 2.10 (m, 4H), 1.84-1.79 (m 2H), 1.43 – 1.25 (m, 24H), -2.45 (t, *J* = 25.9 Hz, 1H).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 157.8.

$^{13}C\{^1H\}$ NMR (101 MHz, toluene-d_8) δ 67.2, 56.8 (t, *J* = 3 Hz), 33.9 (t, *J* = 14 Hz), 33.3 (t, *J* = 16 Hz), 18.6 (t, *J* = 3 Hz), 18.1 (t, *J* = 2 Hz), 17.9, 17.6.(CO signals were not detected)

Complex **1e".**

^1H NMR (400 MHz, toluene-d_8): δ 3.57-3.47 (m, 2H), 3.23-3.15 (m, 2H), 2.38-2.29 (m, 2H), 2.20 – 2.10 (m, 4H), 1.84-1.79 (m 2H), 1.43 – 1.25 (m, 24H), -2.07 (t, *J* = 28.8 Hz, 1H).

$^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8): δ 153.5.

General procedure for hydrogenation reactions.

In an argon filled glove box, an autoclave was charged with complex **1b** (6.6 mg, 0.5 mol%) and toluene (2.0 mL), followed by ketone (2 mmol) and *t*BuOK (2.2 mg, 1.0 mol%), in this order. The autoclave was then charged with H_2 (50 bar). The mixture was stirred for 20 h at 120 °C in an oil bath. The solution was then diluted with ethyl acetate (2.0 mL) and filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate (5 mL). The filtrate was evaporated and the crude residue was purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate as eluent). For specific conditions, see in the main article. For the characterization of the product of the catalysis, see the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

NMR spectra giving characterization of complexes and products of catalysis, X-Ray data tables. Complete details of the X-ray analyses reported herein have been deposited at the Cambridge Crystallographic Data Center (CCDC 1815476-1815481). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, UK; fax: +44 1223 336033.

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

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