

Article

Catalytic Activity of Rhenium(I) Tricarbonyl Complexes Containing Polypyridine and Phosphorus–Nitrogen Ligands in the Hydrogen Transfer of Acetophenone

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Abstract

This work reports the synthesis and characterization of a novel rhenium(I) complex incorporating a phosphorus–nitrogen (P,N) ligand. The compound crystallizes in a distorted octahedral geometry, as confirmed by single-crystal X-ray diffraction analysis. The complexes were evaluated as catalysts in the transfer hydrogenation of acetophenone using 2-propanol as the hydrogen source. Comparative studies with other rhenium(I) complexes bearing polypyridine ligands revealed high catalytic performance, achieving conversions between 68% and 99%. These results highlight the promising potential of P,N-ligand rhenium complexes in homogeneous transfer hydrogenation catalysis. The optimal reaction time was found to be 4 h for the complexes studied, with only the *fac*-[Re(CO)₃(PN)Cl] complex showing improved conversion upon extending the reaction time to 7 h, likely due to the donor effects provided by the P,N-ligand.

Keywords: rhenium(I) tricarbonyl complex; phosphorus-nitrogen ligands; transfer hydrogenation catalysis

1. Introduction

Over the past several decades, the synthesis and design of transition metal complexes featuring pyridine-derived and hetero-bidentate phosphorus-nitrogen (P,N) ligands [1–3]

have garnered significant interest due to their diverse applications in various fields of chemistry [4–6]. Among these, rhenium carbonyl complexes are particularly promising, owing to their potential utility in areas such as microscopy, light-emitting diodes (OLEDs) [7–9], luminescence-based materials [10–13], photosensitizers in solar cells [14], sensors, and biomedical technologies. These applications are largely attributed to their unique photo-physical and photochemical properties, which can be finely tuned through appropriate ligand design [15–19]. Moreover, rhenium complexes have been extensively explored in the context of electrocatalytic and photocatalytic CO₂ reduction [20–24].

Transition metal complexes are also widely recognized for their catalytic activity in transfer hydrogenation (TH) reactions involving ketones and imines [25–29]. Significant advances have been made using catalysts based on ruthenium [30–38], rhodium [39–41], iron [42], and iridium [43–46]. In transfer hydrogenation, a hydrogen atom is delivered from a donor molecule—typically an alcohol—to a substrate, rather than using molecular hydrogen. The mechanism of hydrogen transfer can vary, often involving the concerted or stepwise transfer of a hydride and proton, and is highly dependent on the nature of the metal center, ligand environment, and reaction conditions [25]. Despite the relatively high cost of some catalysts, TH reactions remain attractive due to their operational simplicity, avoidance of pressurized hydrogen gas, and high efficiency under mild conditions.

Rhenium(I) complexes bearing polypyridine or phosphorus-based ligands have been comparatively less explored in the context of TH catalysis. Notably, Landwehr et al. [47] reported the synthesis and catalytic evaluation of [Re(H)(NO)(PR₃)(C₅H₄OH)] complexes in the transfer hydrogenation of ketones and imines using 2-propanol as a hydrogen donor.

This article reports the catalytic activity of a series of Re(I) complexes containing either a polypyridine ligand or a phosphorus–nitrogen (PN) ligand in the hydrogen transfer reaction. The hydrogen transfer was performed using acetophenone as the substrate, and the conversion was studied at different reaction times. In addition, the article describes the synthesis and characterization of a new *fac*-[Re(CO)₃(PN)Cl] complex. The rhenium complexes exhibited catalytic activity in the hydrogen transfer of acetophenone, achieving conversions between 68% and 99% after 7 h of reaction. The results suggest that when coordinated to a Re(I) carbonyl precursor, the ligands promote the hydrogen transfer reaction due to their donor effect.

2. Experimental Section

2.1. General Procedure

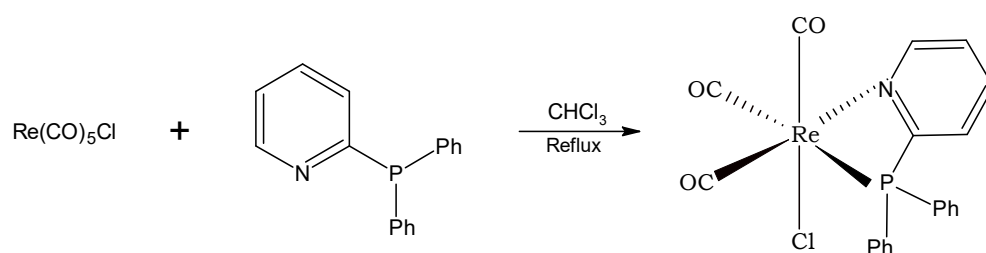
All reactions were carried out under an argon atmosphere. Organic solvents were dried using standard procedures prior to use. [Re(CO)₅Cl] and diphenyl-2-pyridylphosphine were purchased from Aldrich and used without further purification. Infrared spectra were recorded using a PerkinElmer FTIR “Spectrum Two” spectrometer (Shelton, CT, USA) equipped with a UATR accessory. Samples were directly placed on the diamond crystal, pressed to 30% of the total supported pressure, and scanned in the range of 4000–500 cm^{−1} with a resolution of 1 cm^{−1}. ¹H and ³¹P{¹H} NMR spectra were acquired on a Bruker AVANCE 400 MHz spectrometer (Billerica, MA, USA). All chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. Elemental analyses were conducted using a CE Instruments EA 1108 elemental analyzer (Cornaredo, Italy). The following rhenium complexes were synthesized according to previously reported procedures: [Re(CO)₃(PyCOOH)₂Cl] [48], [Re(CO)₃(bpy)Cl] [49], [Re(CO)₃(Phen)Cl] [50], [Re(CO)₃(Phen-NO₂)Cl] [51], [Re(CO)₃(dppz-NO₂)Cl] [51], and [Re(CO)₃(dppz-CN)Cl] [52,53].

Catalytic tests were conducted under a nitrogen atmosphere in a 30 mL glass reactor equipped with a reflux condenser. Typically, the rhenium complex (0.01 mmol) was

dissolved in 2-propanol (8 mL) and heated to reflux under vigorous stirring. Sodium hydroxide (1 mL, 0.1 M) was then added dropwise, followed by acetophenone (10 mmol). The catalytic reaction's progress was monitored by gas chromatography (GC), with periodic sampling being performed every 10 min. GC analysis was carried out with a Pekin Elmer Clarus 580 chromatograph instrument (Shelton, CT, USA) equipped with an FID detector, using an Elite-5 capillary column and nitrogen as carrier gas. The GC analyses were carried out using an internal standard to establish the linearity between the conversion percentage and the concentration of the products formed in the catalytic reaction. GC-mass spectra were run to confirm the identity of the products on a MAT 95 XP Thermo Electron (Bremen, Germany).

2.2. Synthesis of *Fac*-[Re(CO)₃(PN)Cl] Complex

Rhenium pentacarbonyl chloride (180 mg, 0.50 mmol) and diphenyl-2-pyridylphosphine (132 mg, 0.50 mmol) were dissolved in chloroform (30 mL) and refluxed for 24 h (Scheme 1). After cooling to room temperature, the solvent was removed under reduced pressure. The resulting solid was redissolved in chloroform (5 mL) and precipitated by the addition of diethyl ether. The precipitate was cooled at 4 °C, filtered, washed with small amounts of cold diethyl ether, and dried under vacuum. Yield: 134 mg (54%). Anal. Calc. for ReC₂₀H₁₄NPO₃Cl: C, 42.22; H, 2.48; N, 2.46. Found: C, 42.77; H, 2.63; N, 2.49%. FT-IR (ATR, cm^{−1}): νC=O = 2022, 1917, 1893. ¹H NMR ((CD₃)₂CO) δ (ppm), J (Hz): 8.90 (d, J = 5.2, 1H-Py), 8.28 (t, J = 7.9, 1H-Py), 8.10 (dd, J = 7.8, 3.5, 1H-Py), 7.92–7.68 (m, 5H aromatic protons), 7.65–7.45 (m, 6H aromatic protons-Py). ³¹P{¹H} NMR ((CD₃)₂CO) δ (ppm): −31.01. Single crystals suitable for X-ray diffraction were grown via vapor diffusion of diethyl ether into a dichloromethane solution of the complex.



Scheme 1. Synthesis of complex *fac*-[Re(CO)₃(PN)Cl].

2.3. X-Ray Crystal Structure Determination for *Fac*-[Re(CO)₃(PN)Cl] Complex

X-ray suitable crystals were obtained as described above. A suitable single crystal was mounted using MiTeGen MicroMounts (Ithaca, NY, USA). Table 1 shows experimental and crystallographic data for the obtained complex. On the other hand, selected bond distances and angles are reported in Table 2. Intensity data were collected at room temperature on a Bruker D8 QUEST diffractometer (Karlsruhe, Germany) equipped with a bidimensional CMOS Photon100 detector (Madison, WI, USA), using graphite monochromated Mo-Kα radiation. The diffraction frames were integrated by means of the APEX3 package and were corrected for absorptions with SADABS. The solution and refinement for the Re(I) complex was carried out with Olex2 [54]. The structure was solved with Patterson Method using the ShelXS software v2018/3 [55]. The complete structures were refined by the full matrix least-squares procedures of the reflection intensities (F²) with the ShelXL [55]. All non-hydrogens were refined with anisotropic displacement coefficients, and all hydrogen atoms were placed in idealized locations.

Table 1. Crystal data and structure refinement for *fac*-[Re(CO)₃(PN)Cl] complex.

Compound	<i>Fac</i> -[Re(CO) ₃ (PN)Cl]
Empirical formula	C ₂₀ H ₁₄ ClNO ₃ Re
Formula weight	568.94
Temperature/K	298
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.3912 (14)
b/Å	12.4141 (16)
c/Å	16.222 (2)
α/°	90
β/°	94.930 (5)
γ/°	90
Volume/Å ³	2084.9 (5)
Z	4
ρ _{calc} /g/cm ³	1.813
μ/mm ^{−1}	6.052
F (000)	1088.0
Crystal size/mm ³	0.3 × 0.256 × 0.152
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.04 to 52.864
Index ranges	−13 ≤ h ≤ 12, −15 ≤ k ≤ 15, −20 ≤ l ≤ 20
Reflections collected	37,744
Independent reflections	4274 [R _{int} = 0.0272, R _{sigma} = 0.0134]
Data/restraints/parameters	4274/15/239
Goodness-of-fit on F ²	1.085
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0165, wR ₂ = 0.0338
Final R indexes [all data]	R ₁ = 0.0213, wR ₂ = 0.0354
Largest diff. peak/hole/e Å ^{−3}	0.58/−0.67

Table 2. Bond distances and angles of the *fac*-[Re(CO)₃(PN)Cl] complex.

Bond Distances (Å)		
Re1-Cl1		2.4817 (7)
Re1-P1		2.4800 (7)
Re1-N1		2.201 (2)
Re1-C1		1.911 (3)
Re1-C2		1.930 (3)
Re1-C3		1.907 (3)
Bond Angles (°)		
P1-Re1-Cl1		84.43 (2)
N1-Re1-Cl1		83.72 (5)
N1-Re1-P1		65.13 (5)
C1-Re1-Cl1		92.82 (9)
C1-Re1-P1		104.54 (9)
C1-Re1-N1		169.32 (10)
C1-Re1-C2		90.16 (15)
C2-Re1-Cl1		93.82 (10)
C2-Re1-P1		165.25 (12)
C2-Re1-N1		100.13 (13)
C3-Re1-Cl1		176.93 (9)
C3-Re1-P1		93.52 (9)
C3-Re1-N1		93.35 (10)
C3-Re1-C1		89.91 (12)
C3-Re1-C2		87.59 (13)

3. Results and Discussion

3.1. Synthesis and Characterization of *Fac*-[Re(CO)₃(PN)Cl] Complex

The new Rhenium(I) complex was prepared by mixing one equivalent of [Re(CO)₅Cl] compound and one equivalent of the diphenyl-2-pyridylphosphine in refluxing chloroform for 24 h, as shown in Scheme 1. The obtained complex is stable in air, white microcrystalline solid, and soluble in common organic solvents. In the structure of the synthesized new rhenium(I) complex, bidentate coordination of the ligand to the metal is proposed. This occurs between the phosphorus atom and the nitrogen atom from the pyridine fragment of the ligand, and a stable four-membered chelate ring is formed.

The complex features a nearly ideal octahedral geometry around the rhenium center, with a facial (*fac*) arrangement of three carbonyl ligands. The characteristic *fac*-tricarbonyl configuration is supported by the IR spectrum, displaying one strong band at 2022 cm^{−1} and two lower-frequency bands at 1917 and 1893 cm^{−1}, consistent with symmetric and asymmetric CO stretching vibrations.

The new rhenium(I) complex was fully characterized by standard spectroscopic methods (¹H and ³¹P{¹H} NMR) and gave satisfactory analysis. In the ³¹P{¹H} NMR spectrum, the coordinated phosphine of *fac*-[Re(CO)₃(PN)Cl] gives rise to a singlet at δ = −31.01 ppm, whereas the free diphenyl-2-pyridylphosphine ligand exhibits a resonance at δ = −4.1 ppm. This significant upfield shift of approximately 27 ppm clearly indicates strong coordination to the rhenium center. The large nuclear shielding observed in the complex is fully consistent with chelation of the P,N ligand, as reported in related Re(I) tricarbonyl complexes containing donor phosphine ligands [56]. This structural assignment is further confirmed by X-ray crystallographic analysis.

3.2. X-Ray Crystallographic Study

The molecular structure of the *fac*-[Re(CO)₃(PN)Cl] complex, complete with an atom-numbering scheme, is illustrated in Figure 1. The compound crystallized in the monoclinic space group P2₁/c. Selected bond lengths and angles pertinent to the structure are presented in Table 2.

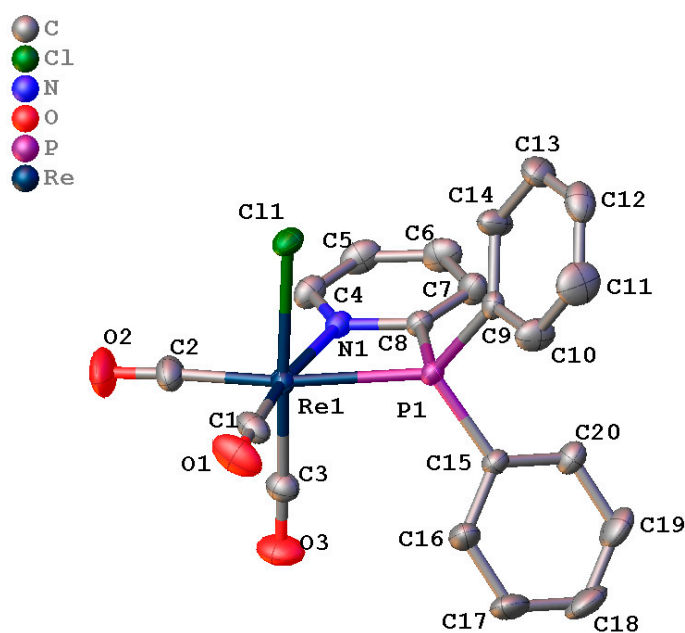


Figure 1. ORTEP of the *fac*-[Re(CO)₃(PN)Cl] complex. The thermal ellipsoids were drawn with a 30% probability. All the hydrogen atoms are omitted for the sake of clarity.

The structural analysis reveals a distorted octahedral coordination sphere with three carbonyl ligands arranged in a *fac* conformation, accompanied by a chloride ligand and the PN bidentate ligand. The bond angles between the carbonyl ligands C1-Re1-C2, C3-Re1-C1, and C3-Re1-C2 are 90.16 (15), 89.91 (12), and 87.59 (13) degrees, confirming the facial conformation. The bite angle of the PN ligand is 65.13 (5), corresponding to the N1-Re1-P1 bond angle; this is the most significant distortion from the ideal octahedral angle (90°) due to the rigidity of the ligand, which results in a deviation of the octahedral distortion parameters. The octahedral deviation parameters for the coordination sphere of *fac*-[Re(CO)₃(PN)Cl] complex is $\Sigma = 77.6 (4)^\circ$ ($(\Sigma = \sum_{i=1}^{12} |\varphi_i - 90|)$ [57] and $\theta = 168.7 (4)^\circ$ [58] parameters $\theta = \sum_{i=1}^{24} |\theta_i - 60|$).

On the other hand, Table 3 shows the intermolecular interactions of the *fac*-[Re(CO)₃(PN)Cl] complex. The crystal structure is stabilized by some weak hydrogen bonds (according to Desiraju's classification). This corresponds to the intermolecular interaction between O1 of the carbonyl ligand and H7 (+x, 3/2 − y, −1/2 + z). Furthermore, it is noted that the Cl1 ligand engages in a dual intermolecular interaction with the hydrogens from the adjacent asymmetric units H6 (+x, 3/2 − y, −1/2 + z) and H5 (2 − x, 1 − y, 1 − z). A Hirshfeld surface analysis was carried out to adequately describe the intermolecular interactions.

Table 3. Intermolecular hydrogen-bonding interaction parameters for compound *fac*-[Re(CO)₃(PN)Cl].

D-H...A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C7 ⁱ -H7 ⁱ ...O1	0.93	2.55	3.347 (4)	143.7
C6 ⁱⁱ -H6 ⁱⁱ ...Cl1	0.93	2.87	3.794 (3)	170.4
C5 ⁱⁱ -H5 ⁱⁱ ...Cl1	0.93	2.87	3.528 (4)	128.6

Symmetry codes: ⁱ (+x, 3/2 − y, −1/2 + z); ⁱⁱ (2 − x, 1 − y, 1 − z).

Hirshfeld Surface Analysis

In this study, the assessment of Hirshfeld surfaces and their corresponding two-dimensional fingerprint plots was conducted employing the CrystalExplorer software v17.5 [59–61]. Input for the analysis was sourced from the crystallographic information file (CIF) pertinent to each molecular complex under investigation.

The intermolecular interactions of the crystal structures of *fac*-[Re(CO)₃(PN)Cl] were quantified using Hirshfeld surface analysis (Figure 2). The more essential contributions of the different interactions are presented in Figure 3. For *fac*-[Re(CO)₃(PN)Cl] complex, the fingerprint plots show that the dominant interaction is H...H (32.1%). In the same way, the complex exhibited a significant O...H contribution (26.3%) corresponding to intermolecular interactions by hydrogen bonds between the oxygen of carbonyl ligands to hydrogen atoms from the C-H aromatic ring (see above). Furthermore, the Cl...H interaction exhibits a percentage of the contribution of 10.7%, corresponding to the weak molecular interaction between the chloro ligand and C-H hydrogen atoms. Finally, the H...C and O...C interactions, accounting for percentages of 17.7% and 10.4%, respectively, represent the C-H...π and CO...π interactions observed within the crystalline arrangement. A detailed description of the methodology and the definition of the d_{norm} parameter, and the full set of fingerprint plots and interaction contributions are provided in the Supplementary Information.

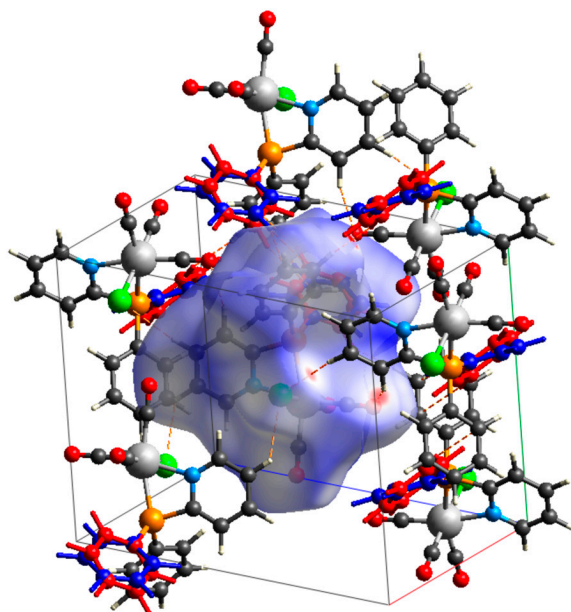


Figure 2. Hirshfeld surface mapped with dnorm over molecular structure of *fac*-[Re(CO)₃(PN)Cl] complex.

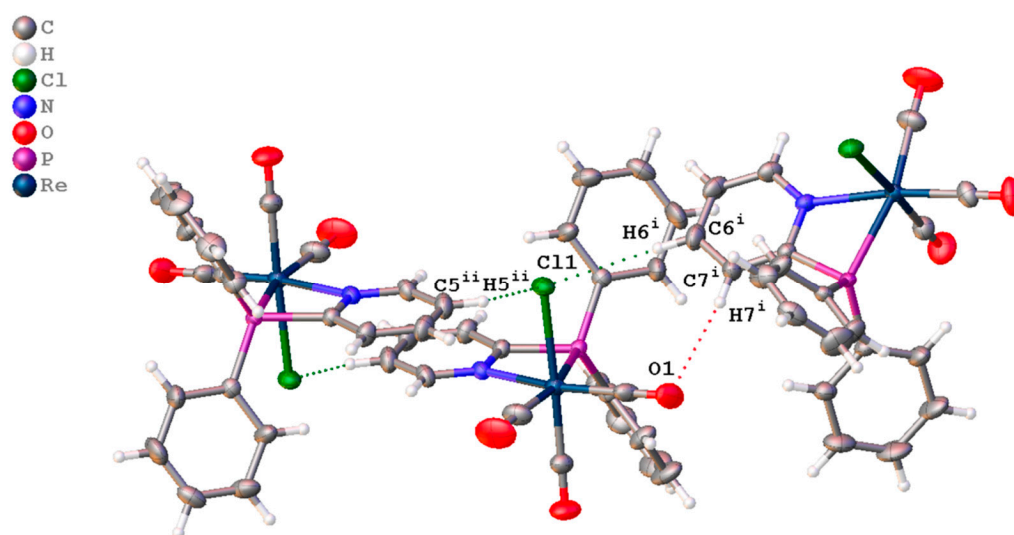
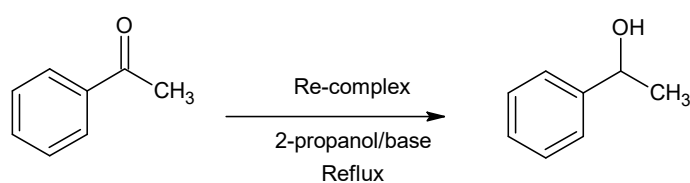


Figure 3. The intermolecular hydrogen bonds of *fac*-[Re(CO)₃(PN)Cl] crystal structure. Symmetry codes: ⁱ (+x, 3/2 − y, −1/2 + z); ⁱⁱ (2 − x, 1 − y, 1 − z).

3.3. Catalytic Activity

Reaction aliquots were taken every 1 h and analyzed by gas chromatography (GC) to determine conversion and selectivity. The hydrogen transfer reaction is illustrated in Scheme 2, and the catalytic results are summarized in Table 4.



Scheme 2. Hydrogenation of acetophenone by a rhenium(I) complex.

Table 4. Transfer hydrogenation of acetophenone catalyzed by Re(I) complexes.

Entry	Complex	% Conversion (TON, TOF h ^{−1})				
		1 h	2 h	3 h	4 h	7 h
1	[Re(CO) ₅ Cl]	3 (30, 30)	7 (70, 35)	8 (80, 27)	8 (80, 27)	8 (80, 27)
2	[Re(CO) ₃ (PN)Cl]	15 (150, 150)	37 (370, 185)	65 (650, 217)	80 (800, 200)	99 (990, 141)
3	[Re(CO) ₃ (PyCOOH) ₂ Cl]	24 (240, 240)	44 (440, 220)	56 (560, 187)	65 (650, 163)	70 (700, 100)
4	[Re(CO) ₃ (bpy)Cl]	33 (330, 330)	53 (530, 265)	70 (700, 233)	88 (880, 220)	90 (900, 129)
5	[Re(CO) ₃ (Phen)Cl]	30 (300, 300)	47 (470, 235)	55 (550, 183)	68 (680, 170)	71 (710, 101)
6	[Re(CO) ₃ (Phen-NO ₂)Cl]	36 (360, 360)	52 (520, 260)	63 (630, 210)	66 (660, 165)	68 (680, 97)
7	[Re(CO) ₃ (dppz-NO ₂)Cl]	34 (340, 340)	65 (650, 325)	71 (710, 240)	68 (680, 170)	69 (690, 98)
8	[Re(CO) ₃ (dppz-CN)Cl]	29 (290, 290)	42 (420, 210)	56 (560, 187)	62 (620, 155)	68 (680, 97)

Condition: Substrate/catalyst = 1000/1; Catalyst = 0.01 mmol; NaOH/metal = 10/1; solvent = 2-propanol; temperature = Reflux.

In homogeneous catalysis, the ligand plays a crucial role not only in stabilizing the metal center but also in modulating the reaction selectivity. In this study, both phosphorus–nitrogen and polypyridine ligands were evaluated, each providing strong donor effects to the rhenium center. For transfer hydrogenation, formation of a metal hydride is generally required for catalytic activity, and such formation is favored when electron-donating ligands are present.

The results in Table 4 indicate that all tested Re(I) complexes were active, achieving conversions between 68% and 99% (after 7 h of reaction time), with 100% selectivity toward the alcohol product. Comparison between the precursor [Re(CO)₅Cl] and its derivatives demonstrate that donor ligands significantly enhance catalytic performance, likely by stabilizing the active metal species under reaction conditions. Without such stabilization, the rhenium center may undergo reduction to Re(0), leading to catalyst deactivation.

Turnover numbers (TONs) suggest gradual deactivation over time, as values do not scale proportionally with reaction duration. Among the tested complexes, [Re(CO)₃(bpy)Cl] and *fac*-[Re(CO)₃(PN)Cl] exhibited the highest activity after 4 h, with turnover frequencies (TOFs) of 220 h^{−1} and 200 h^{−1}, respectively. The complex [Re(CO)₃(bpy)Cl] does not increase its activity when the reaction time is extended to 7 h, however complex *fac*-[Re(CO)₃(PN)Cl] shows a conversion of 99% when the reaction time is extended. This suggests that the complex [Re(CO)₃(bpy)Cl] undergoes deactivation after 4 h of reaction, this is confirmed by the low increase in TON, which rises from 650 to only 700. All catalysts show maximum activity after 4 h of reaction, and only complex *fac*-[Re(CO)₃(PN)Cl] shows a significant increase when the reaction time is 7 h. The activity for the complex *fac*-[Re(CO)₃(PN)Cl] improves from 80% to 99%. This could indicate that the donor effects of this ligand stabilize the complex *fac*-[Re(CO)₃(PN)Cl] under the reaction conditions studied. An experiment was designed to detect the Re–H species by ¹H NMR spectroscopy. However, it was not possible to characterize this intermediate, most likely because the Re–H species decomposes rapidly, as suggested by the bubbling observed when transferring the sample from the reactor to the NMR tube. In contrast, our group has successfully detected other transition metal hydrides, such as ruthenium complexes, which are more stable and can be characterized by NMR [62].

For comparison, Landwehr et al. [47] reported 98% conversion in only 1 h using [Re(H)(NO)(PR₃)(C₅H₄OH)] (R = iPr₃, Cy) as catalyst in acetophenone transfer hydrogenation. However, their experiments employed a substrate-to-catalyst ratio of 200:1, whereas our study used a ratio of 1000:1 (five times higher) yielding comparable TOFs. This ob-

servation reinforces that rhenium carbonyl complexes require initial hydride formation to become catalytically active under mild conditions.

In addition to the catalytic performance, the solubility and stability of the rhenium(I) complexes were evaluated. The complexes are soluble under the catalytic conditions employed, with an estimated solubility of ca. 10 mg/15 mL of isopropanol. This level of solubility was sufficient to carry out the catalytic reactions efficiently and ensured the reproducibility of the experimental results. Furthermore, the complexes exhibited good stability under transfer hydrogenation conditions. As shown in Table 4, the turnover numbers (TONs) increase consistently with reaction time, indicating that the catalysts remain active throughout the reaction with only minor loss of activity. These observations confirm that both solubility and stability contribute to the reliable catalytic performance of the complexes studied.

Overall, the rhenium complexes studied here, particularly those with strong donor ligands, demonstrate promising activity and selectivity in transfer hydrogenation, while offering advantages over noble metal catalysts such as ruthenium and rhodium in terms of cost and ease of synthesis.

4. Conclusions

We have developed a synthetic procedure for obtaining a novel rhenium(I) tricarbonyl complex incorporating a phosphorus–nitrogen ligand (PN = diphenyl-2-pyridylphosphine). The resulting compound, *fac*-[Re(CO)₃(PN)Cl], crystallizes in a distorted octahedral geometry, as confirmed by single-crystal X-ray diffraction analysis.

Catalytic studies demonstrated that *fac*-[Re(CO)₃(PN)Cl] is an effective homogeneous catalyst for the transfer hydrogenation of acetophenone using 2-propanol as a hydrogen donor. High conversion (99%) and complete selectivity (100%) toward the alcohol product were achieved under mild conditions, with a substrate-to-catalyst ratio of 1000:1. Comparable activity was observed for the polypyridine complex [Re(CO)₃(bpy)Cl], which exhibited turnover frequency of TOF (220 h^{−1}) and the *fac*-[Re(CO)₃(PN)Cl] (200 h^{−1}) reported at 4 h of reaction time.

The catalytic performance of these rhenium complexes, particularly given the high substrate-to-catalyst ratio, is in line with previously reported systems employing more noble metals, while offering advantages in terms of cost and accessibility. The combination of ease of synthesis, structural stability, and high activity highlights P,N- and polypyridine-ligated rhenium(I) complexes as promising candidates for sustainable homogeneous transfer hydrogenation catalysis.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics13100338/s1>, Figure S1: ¹H NMR spectrum of *fac*-[Re(CO)₃(PN)Cl] in acetone-d₆; Figure S2: ³¹P{¹H} NMR spectrum of *fac*-[Re(CO)₃(PN)Cl] in (CD₃)₂CO; Figure S3: FT-IR spectrum of *fac*-[Re(CO)₃(PN)Cl]; Figure S4: FT-IR spectrum of [Re(CO)₃(bpy)Cl]; Figure S5: ¹H NMR spectrum of *fac*-[Re(CO)₃(Phen)Cl] in CDCl₃; Figure S6: FT-IR spectrum of *fac*-[Re(CO)₃(Phen)Cl]; Figure S7: ¹H NMR spectrum of *fac*-[Re(CO)₃(Phen-NO₂)Cl] in CDCl₃; Figure S8: FT-IR spectrum of *fac*-[Re(CO)₃(Phen-NO₂)Cl]; Figure S9: ¹H NMR spectrum of *fac*-[Re(CO)₃(dppz-NO₂)Cl] in DMSO-d₆; Figure S10: FT-IR spectrum of *fac*-[Re(CO)₃(dppz-NO₂)Cl]; Figure S11: ¹H NMR spectrum of *fac*-[Re(CO)₃(dppz-CN)Cl] in CDCl₃; Figure S12: FT-IR spectrum of *fac*-[Re(CO)₃(dppz-CN)Cl]; Figure S13: ¹H NMR spectrum of *fac*-[Re(CO)₃(PyCOOH)₂Cl] in (CD₃)₂CO; Figure S14: FT-IR spectrum of *fac*-[Re(CO)₃(PyCOOH)₂Cl]. Figure S15: Full set of 2D fingerprint plots of *fac*-[Re(CO)₃(PN)Cl] complex for intermolecular contacts. Supplementary data CCDC reference number 1584232 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures> (accessed 12

October 2025) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44 1223/336 033; Email: deposit@ccdc.cam.ac.uk.

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