New Chiral Ferrocenylamine Sulfide and Selenide Ligands: Preparation, Characterization and their Palladium and Platinum Complexes as Catalysts for Selective Hydrogenation

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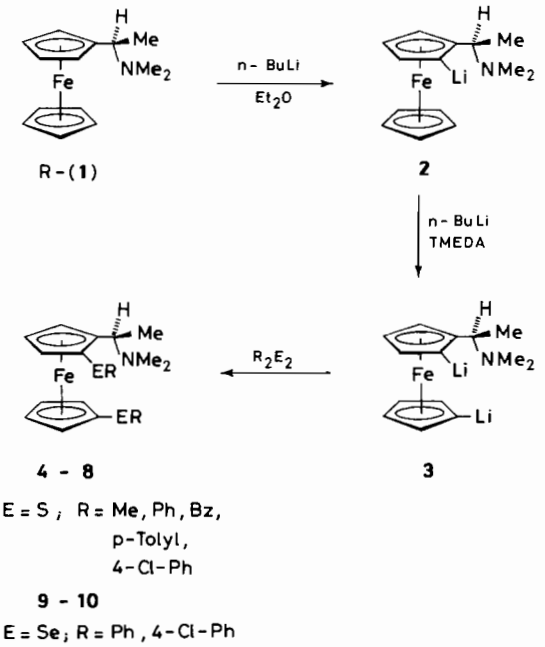
Abstract

A series of new ferrocenylamine sulfides and selenides, (*R,S*)-(C_5H_3-1-CHMeNMe$_2$-2-ER)Fe(C_5H_4-ER), (E = S; R = Me, Ph, Bz, 4-tolyl and 4-chlorophenyl and E = Se; R = Ph and 4-chlorophenyl) have been prepared by the lithiation of (*R*)-*N,N*-dimethyl-1-ferrocenylethylamine, first in the presence of ether and then TMEDA followed by reaction with the appropriate disulfides or diselenides. These compounds react with $(PhCN)_2MCl_2$, M = Pd, Pt to form new heterobimetallic complexes, (*R,S*)-(C_5H_4-ER)Fe(C_5H_3-1-CHMeNMe$_2$-2-ER)MCl_2, (E = S, Se; R = Me, Et, n-Pr, i-Pr [1], Ph, Bz, 4-tolyl and 4-chlorophenyl; M = Pd, Pt). The following techniques were used for characterization: ^1H and ^{13}C NMR, IR, MS and elemental analysis. The possible structure for the bimetallic complexes is discussed. The palladium ferrocenyl complexes are effective catalysts for selective hydrogenation of dienes to monoenes under homogeneous conditions.

Introduction

Recently, we reported the preparation, characterization and use in catalytic processes of ferrocenylamine sulfide and selenide metal complexes [1–5]. In this work we report the synthesis of a new series of chiral ligands (*R,S*)-(C_5H_4-ER)Fe(C_5H_3-1-CHMeNMe$_2$-2-ER), where E = S, Se and R = Me, Ph, Bz, 4-tolyl and 4-chlorophenyl. These compounds have been prepared by stepwise lithiation with n-BuLi of the resolved amine **1** [6] in the presence of ether and then TMEDA followed by treatment with appropriate RS-SR or RSe–SeR (Scheme 1). These ligands chelate palladium and platinum dichloride and produce the desired complexes of the type (*R,S*)-(C_5H_4-ER)Fe(C_5H_3-1-CHMeNMe$_2$-ER)MCl_2. The palladium complexes are selective catalysts for the reduction of conjugated dienes to monoenes.



Scheme 1.

Experimental

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere. Standard Schlenk-ware techniques and a vacuum line were employed. All solvents used were reagent grade and were distilled by standard methods [7]. Bis(benzonitrile)metal complexes [$(PhCN)_2MCl_2$], where M = Pd, Pt were prepared according to the reported procedure [8].

^1H and ^{13}C NMR were obtained by use of a Bruker WM-250 spectrometer. Mass spectra were obtained by use of a Finnigan 4000 instrument with an Incos Data system at 70 eV. Infrared spectra were recorded by means of a Perkin-Elmer 599 spectrophotometer by using neat films for liquid samples and Nujol mull between CsI plates or in KBr pellets. Elemental analyses were performed

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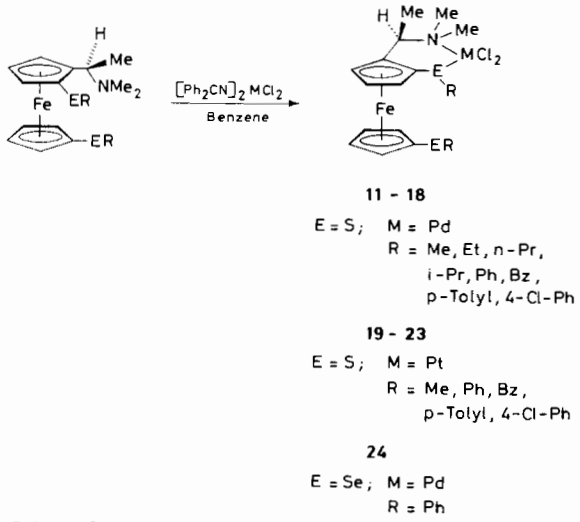
by Galbraith Laboratory, Knoxville, TN. Gas chromatography (GC) was carried out by using a Hewlett-Packard 5880A instrument with a 25 m GB-1 Capillary Column, and a Varian 1400 instrument with 30 m DBWAX MEGABORE Column. All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. The (1,3-cyclooctadiene + cyclooctene):cyclooctane and 1,3-cyclohexadiene:cyclohexene:cyclohexane ratios in hydrogenation were determined by GC. The 1,3-cyclooctadiene:cyclooctene ratios were determined by integration of the olefinic region of the ^1H NMR spectra.

Preparation of Ligands

A 2.7 M solution of n-BuLi in hexane (2.0 ml, 5.4 mmol) was added dropwise to a solution of (*R*)-[1-(dimethylamino)ethyl]ferrocene [(*R*)-**1**] (1.3 g, 5.1 mmol) in 50 ml dry ether at −78 °C under Ar. After being stirred for 8 h, a mixture of freshly distilled TMEDA (0.65 g, 5.4 mmol) and 2.7 M n-BuLi (2.0 ml, 5.4 mmol) was transferred into the reaction flask at −78 °C and the reaction mixture was stirred for another 8 h. A solution of R_2S_2 or R_2Se_2 (11 mmol) in 20 ml ether was added dropwise to the reaction mixture at −78 °C over a 20 min period and stirred for another 24 h. The mixture was then hydrolyzed with 50 ml saturated aqueous $NaHCO_3$. The resulting organic layer and ether extracts from the aqueous layer were combined, washed twice with ice water, dried over anhydrous K_2CO_3 and concentrated to give a dark, oily residue that was chromatographed on silica gel by eluting first with hexane and then ether to give the product. Upon recrystallization from CH_2Cl_2/hexane, crystals were obtained.

Preparation of Metal Complexes

Complexes **11**–**24** (Scheme 2) were prepared from benzene solutions of 0.1 g $(PhCN)_2PdCl_2$ or 2.0 g $(PhCN)_2PtCl_2$ and a slight excess of ligands in an approximate 1:1.2 molar ratio. The reaction mixture was stirred for 8 h in the case of Pd complexes and for five days in the case of Pt complexes.



11 - 18

E = S; M = Pd
R = Me, Et, n-Pr, i-Pr, Ph, Bz, p-Tolyl, 4-Cl-Ph

19 - 23

E = S; M = Pt
R = Me, Ph, Bz, p-Tolyl, 4-Cl-Ph

24

E = Se; M = Pd
R = Ph

Scheme 2.

The resulting precipitates were collected by filteration, washed with cold benzene and petroleum ether. The pure crystals were obtained by recrystallization from CH_2Cl_2/hexane for Pd complexes and acetone for Pt complexes.

Homogeneous Hydrogenation of 1,3-Cyclooctadiene and 1,3-Cyclohexadiene by Using Palladium and Platinum Complexes

The palladium or platinum complexes (**11**–**24**), solvent and 1,3-cyclooctadiene or 1,3-cyclohexadiene were added to a 100 ml pressure bottle equipped with pressure gauge and stirring bar. The bottle was evacuated and filled several times with H_2 to the desired pressure (102 psi). The initial turnover rate, product analysis at the end of reaction and the selectivity were determined.

Results and Discussion

New ferrocenylamine sulfide and selenide ligands **4**–**10** have been prepared via lithiation of (*R*)-[1-(dimethylamino)ethyl]ferrocene followed by reaction

TABLE 1. Microanalytical data for ligands **4**–**10**

Compound	Yield (%)	Color	Melting point (°C)	Analysis: found (calc.) (%)	
				C	H
4	92	brown	oil	55.65(55.01)	6.08(6.04)
5	77	yellow	74–75	65.61(65.96)	5.77(5.75)
6	54	brown	oil	66.95(67.06)	6.44(6.23)
7	72	yellow	89–90	66.86(67.06)	6.21(6.23)
8	76	yellow	101–102	57.53(57.59)	4.67(4.65)
9	72	brown	oil	55.18(55.05)	4.97(4.80)
10	69	yellow	45–46	49.32(49.09)	3.95(3.96)

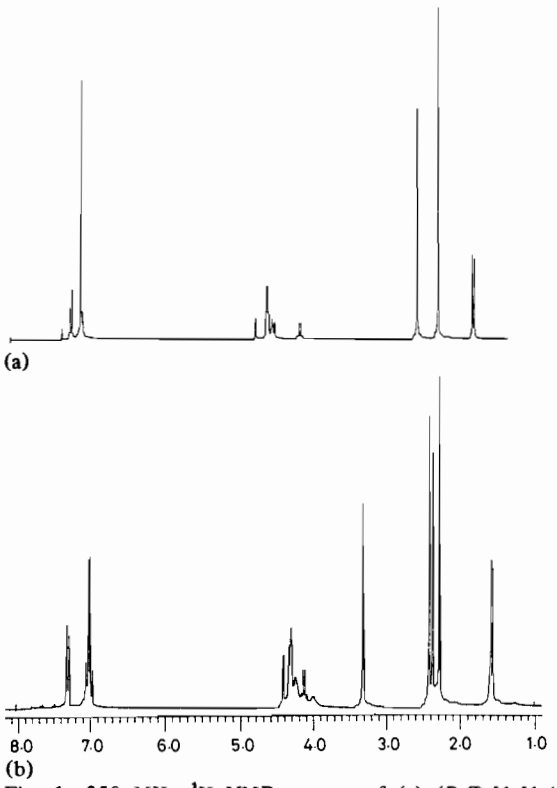


Fig. 1. 250 MHz ^{1}H NMR spectra of (a) (*R,S*)-[1-[1-(dimethylamino)ethyl]-2,1′-bis[(4-tolyl)thio]ferrocene] (7); (b) (*R,S*)-[1-[1-(dimethylamino)ethyl]-2,1′-bis[(4-tolyl)thio]-ferrocene] palladium dichloride (17).

with different disulfides or diselenides as shown in Scheme 1. Analytical results, yields and melting points of these ligands are given in Table 1.

These compounds are chiral molecules with two elements of chirality, central and planar. The procedure of Gokel and Ugi [6] was used for preparation of (*R*)-amine **1**. This enantiomer is stereoselectively lithiated by n-BuLi to give 96% of (*R,R*)-**2** (Scheme 1) [9]. Further lithiation with n-BuLi in the presence of TMEDA yields (*R,R*)-**3** in high enantiomeric excess. The products **4**–**10** are separated by gradient elution chromatography on a silica gel column.

Figure 1(a) shows the ^{1}H NMR spectrum of **7**. The nitrogen methyls appear as singlets in these compounds because the inversion of the pyramidal nitrogen of NMe_2 is faster than the NMR time scale at room temperature. These singlet peaks are generally upfield due to the ring-current effect.

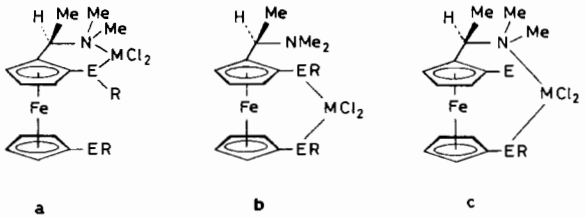
For the 250 MHz ^{13}C NMR data of ligands **4**–**10** see 'Supplementary Material'. ^{13}C NMR of compound **7**, a typical example is as follows: 12.3 (q, CH*Me*); 20.8 (q, Ph-*Me*); 40.2 (q, N*Me*$_2$); 56.2 (d, *C*HMe); 77.2 (d, C_3', C_4'); 73.4 (d, C_2', C_5'); 73.6 (d, C_2', C_5'); 70.4 (d, C_3, C_4C_5); 70.6 (d, C_3, C_4, C_5); 77.7 (d, C_3, C_4, C_5); 79.4 (S, C_1', C_2); 80.1 (S, C_1', C_2); 95.4 (S, C_1); 127.6 (d, *ortho*-Ph); 128.6 (d, *ortho*-Ph); 129.8 (d, *meta*-Ph); 130.3 (d, *meta*-Ph); 135.5 (s, *para*-Ph); 135.8 (s, *para*-Ph); 137.5 (S, substituted-Ph). The two methyl groups of NMe_2 are diastereotopic and, therefore, non-equivalent. They give only one signal because of rapid inversion at the N atom as stated previously. Assignment of Cp carbons is difficult and tentative. Koridze and co-workers [10] have assigned the signals in methoxyferrocene on the basis of deuterium labeling studies. In this work such labeling studies have not been performed. However, the assignment of C_1, C_2 and C_1' are clear. With the exception of the aryl carbons, the three most downfield peaks are due to substituted ring carbons C_1, C_2 and C_1'. The chemical shifts of C_2 and C_1' reflect the inductive and the field effect of the substituents (–SeR) and (–SR) and they should be close to each other. Two adjacent peaks in region 77–86 ppm belong to C_2 and C_1'. C_1 has greater shift in the region of 93–96 ppm. Assignment of other carbons on the Cp rings is based on comparison with previous results [1–5]. The mass spectra show molecular ions and anticipated fragments. Smaller peaks consistent with different isotopes of Fe, S and Se are also observed. The mass spectrum of compound **7** is a typical example; MS, *m/e* (relative intensity) 501 (59, M^+), 486 (22, M^+ – Me), 456 (35, M^+ – 3Me), 429 (19, M^+ – CHMe-NMe_2), 72 (100, CHMeNMe_2), 56 (24, Fe), 44 (24, NMe_2).

Palladium and platinum complexes **11**–**24** have been made by reaction of ferrocenylamine sulfide and selenide ligands with bis(benzonitrile)dichloride palladium or platinum(II) in benzene solution (Scheme 2). These heterobimetallic complexes are insoluble in benzene. Pure samples can be obtained by recrystallization from CH_2Cl_2/hexane in the case of palladium complexes and from acetone in the case of platinum complexes.

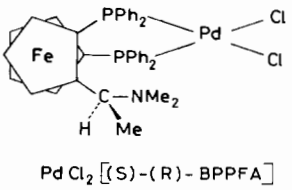
Microanalytical data, yields and melting points of compounds **11**–**24** are presented in Table 2. Figure 1(b) shows the ^{1}H NMR spectrum of compound **17** which has been synthesized from ligand **7** upon complexation with palladium chloride. Figure 1 indicates the differences between the NMR spectra of the free ligand **7** and its palladium complex **17**. Comparison of these two spectra is important to deduce the structure of the metal complexes. Ligands **4**–**10** have three coordination sites, N and two S (or Se) atoms. Therefore, there are three possible structures as shown in Scheme 3. The structure of $PdCl_2$[(*S*)-(*R*)-BPPFA] has been reported by Kumada and co-workers [11] (Fig. 2). In that complex palladium is coordinated by both phosphine atoms, rather than coordinated by a phosphine and nitrogen atom. However, the following results rule out the existence of a similar structure for the analog, ferrocenylamino sulfide and

TABLE 2. Yield, melting point, color, analytical data of complexes **11–24**

Compound	Yield	Color	Melting point (°C, dec.)	Analysis: found (calc.) (%)	
				C	H
11	92	dark purple	146–148	36.34(36.49)	4.78(4.40)
12	52	purple	136–137	38.55(38.98)	4.91(4.91)
13	61	brown	147–148	41.44(41.22)	5.31(5.36)
14	55	brown	150–151	42.23(41.22)	5.44(5.36)
15	85	red	137–138	47.73(47.99)	4.15(4.18)
16	71	purple	173–175	49.47(49.54)	4.45(4.60)
17	82	dark red	160–162	49.89(49.54)	4.54(4.60)
18	93	black	157–159	43.51(43.42)	3.55(3.50)
19	54	yellow	166–168	31.01(31.23)	3.86(3.77)
20	58	yellow	191–192	42.29(42.23)	3.64(3.68)
21	53	yellow	175–177	43.97(43.82)	4.09(4.07)
22	65	yellow	193–194	43.61(43.82)	4.25(4.07)
23	75	yellow	210–212	42.29(42.23)	3.69(3.68)
24	89	red	164–166	41.11(41.90)	3.92(3.66)



Scheme 3.



PdCl2[(S)-(R)-BPPFA]

Fig. 2. Structure of $PdCl_2$[(*S*)-(*R*)-BPPFA].

selenide complexes. (i) The non-isochronicity of the two methyl groups of NMe_2 (Fig. 1(b) and Table 7; Table 9 (Supplementary Material)) is strong evidence for coordination of that group to the metal as a consequence of a higher energy barrier for inversion at the nitrogen atom. However, coordination of the sulfur substituent on the second Cp ring cannot be ruled out (Scheme 3, c). (ii) An X-ray structure study for a similar palladium complex, $(C_5H_4\text{-}SMe)Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SMe)\text{-}PdCl_2$, has been undertaken [12] and has confirmed that the metal complexes have structure a (Scheme 3).

Hydrogenation

Hydrogenation by homogeneous catalysts of palladium and platinum have been used with varying degrees of success [13]. The complexes, formed from the reaction of palladium chloride and thioethers, are selective catalysts after reduction by di-isobutylaluminum hydride [14]. Active and selective catalysts were prepared upon treatment of $PdCl_2$ or Na_2PdCl_4 with tertiary amines [15] or reaction of $PdCl_2$ with 2,2′-bipyridine and $NaBH_4$ [16]. It was found that in the presence of $SnCl_2$, $PtCl_2(SPh_2)_2$ is a selective homogeneous catalyst for reduction of a diene to a monoene [17]. Homogeneous and heterogeneous hydrogenation of a diene to a monoene was previously reported by this laboratory [2–4]. In order to investigate the activity of new palladium and platinum complexes as selective catalysts and compare this activity with other ferrocenylamine sulfide compounds, 1,3-cyclooctadiene and 1,3-cyclohexadiene were hydrogenated with different complexes in various solvents at room temperature. Table 3 shows the results of hydrogenation of 1,3-cyclooctadiene with various complexes in acetone. As illustrated in Table 3, homogeneous hydrogenation proceeds at a high rate (645.1 mol/mol of Pd per h) with high yields (100% conversion in most cases) and excellent selectivity (up to 100%). A direct comparison of compound **18** which has two 4-chlorophenyl sulfide substituents on both Cp rings, with the analog **25** [18] which has only one 4-chlorophenyl sulfide substituent, shows a better turnover rate and higher selectivity for the former complex. No hydrogen uptake was observed when complexes **20** with Pt–S and **24** with Pd–Se were used. A possible explanation is that the Pd–S bond is weaker than either Pt–S or Pd–Se and breakage of this Pd–S bond may be important to the selective hydrogenation of the 1,3-cyclooctadiene. Table 3 also shows that catalysts with alkyl substituents of thioether have higher selectivities and those with aryl

TABLE 3. Selective hydrogenation of 1,3-cyclooctadiene[a] with various complexes, (*R,S*)-(C_5H_4-ER)Fe(C_5H_3-1-CHMeNMe_2-2-ER)MCl_2, in acetone[b] at 102 psi hydrogen pressure

Catalysts	Conversion (%)	Induction time (h)	Turnover rate (mol/mol cat. h)	Products (%)		Selectivity[c]
				Cyclooctene	Cyclooctane	
11 R = Me; E = S; M = Pd	100	0	45.7	95.5	4.5	95.5
12 R = Et; E = S; M = Pd	100	0	9.70	100	0.0	100
13 R = n-Pr; E = S; M-Pd	100	0	18.3	92.3	7.7	92.3
15 R = Ph; E = S; M = Pd	100	0	114.5	86.4	13.6	86.4
16 R = Bz; E = S; M = Pd	100	0	62.4	89.7	10.3	89.7
17 R = *p*-tolyl; E = S; M = Pd	100	0	291.9	84.6	15.4	84.6
18 R = 4-ClPh; M = Pd	100	0	645.1	91.6	8.43	91.6
20 R = Ph; E = S; M = Pt				No H_2 Uptake		
24 R = Ph; E = Se; M = Pd				No H_2 Uptake		
25[d]	100	0.5	353.0	87.6	12.4	87.6

[a] 7.45×10^{-3} mol of substrate. [b] 9 ml of solvent. [c] Cyclooctane/(cyclooctene + cyclooctane). [d] Compound **25** is CpFe[C_5H_3-1-CHMeNMe_2-2-S(Ph-Cl)]PdCl_2 [18].

TABLE 4. Hydrogenation of 1,3-cyclooctadiene[a] with [C_5H_4-S(4-Cl-Ph)]Fe[C_5H_3-1-CHMeNMe_2-2-S(4-Cl-Ph)]PdCl_2 (**18**) in different solvents[b] at 102 psi hydrogen pressure

Catalyst	Solvent	Turnover rate (mol/mol cat. h)	Conversion (%)	Products (%)		Selectivity[c]
				Cyclooctene	Cyclooctane	
18	acetone	645.1	100	91.6	8.43	91.6
18	THF	371.6	95.0	84.6	10.4	89.1
18	pyridine	82.1	7.23	7.23	0.0	100
18	CH_2Cl_2	165.6	93.8	92.2	1.55	98.3

[a] 7.45×10^{-3} mol of substrate. [b] 9 ml of solvent, at room temperature. [c] Cyclooctene/(cyclooctene + cyclooctane).

substituents have higher turnover rates. Table 4 shows the solvent-effect in homogeneous hydrogenation of 1,3-cyclooctadiene with catalyst **18**. Acetone has the highest turnover rate and highest conversion. In contrast, when pyridine was used as a solvent, the highest selectivity was obtained but conversion was low. These results clearly show that here solvents play a major role in hydrogenation. Table 5 shows the result of the hydrogenation of 1,3-cyclohexadiene. This reaction has been carried out with high yield, normal reaction rate and excellent selectivity. Comparison between the hydrogenation of 1,3-cyclooctadiene and 1,3-cyclohexadiene (Tables 3 and 5) shows that for the two ligands investigated selectivity is higher for the latter substrate, regardless of catalysts. However, the turnover rate strongly depends on the catalysts. In order to evaluate the activity of the complexes reported here, catalyst **18** is compared with previously known Pd complexes (Table 6). Comparison of this catalyst (entries

TABLE 5. Hydrogenation of 1,3-cyclohexadiene[a] with various catalysts at room temperature and 102 psi hydrogen pressure

Catalyst[b]	Turnover rate (mol/mol cat. h)	Conversion (%)	Products (%)		Selectivity[c]
			Cyclohexene	Cyclohexane	
15	249.5	100	97.0	3.05	97.0
18	248.3	100	95.7	4.31	95.7

[a] 7.45×10^{-5} mol of substrate in 9 ml acetone, at 102 psi. [b] 2×10^{-5} mol catalysts. [c] Cyclohexene/(cyclohexene + cyclohexane).

TABLE 6. Selective hydrogenation of dienes to monoenes, comparison of the catalytic activity of new complexes with previously known Pd catalysts

Initial rate (mol/mol of Pd/h/psi)	Substrate	T (°C)	Solvent	Additive	Reference
6.32	1,3-cyclooctadiene	27	acetone		this work[a]
2.43	1,3-cyclohexadiene	27	acetone		this work[a]
8.99	1,3-cyclooctadiene	22	toluene	water	16
3.45–5.52	isoprene	22	toluene		15
0.0011	1,4-cyclohexadiene	65	toluene		19

[a] Catalyst **18**, $[C_5H_4\text{-}S(Ph\text{-}Cl]Fe[C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2S(Ph\text{-}Cl)]PdCl_2$.

1 and 2) and the third entry ($PdCl_2$ complexed by undecylamine, reduced by di-isobutylaluminum hydride and hydrolyzed) [16] shows the same order of magnitude for the rate of hydrogenation of 1,3-cyclooctadiene and 1,3-cyclohexadiene. This catalyst appears to be almost as fast as the amine catalyst in entry 4 [15] and by three orders of magnitude faster than the chelating bis(phosphine) (entry 5) [19].

Supplementary Material

Tables of ^1H and ^{13}C NMR data (3 pages) are available from the authors on request.

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