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Journal of Organometallic Chemistry 692 (2007) 5272–5278
Journal of Organometallic Chemistry
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N-Acetyl-*N*,*N*-dipyrid-2-yl (cyclooctadiene) rhodium (I) and iridium (I) complexes: Synthesis, X-ray structures, their use in hydroformylation and carbonyl hydrosilylation reactions and in the polymerization of diazocompounds

Bhasker Bantu [a], Klaus Wurst [b], Michael R. Buchmeiser [a,c,*]

[a] *Leibniz-Institut für Oberflächenmodifizierung e.V. (IOM), Permoserstraße 15, D-04318 Leipzig, Germany*
[b] *Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*
[c] *Institut für Technische Chemie, Universität Leipzig, Linnéstr. 3, D-04103 Leipzig, Germany*

Received 30 April 2007; received in revised form 6 August 2007; accepted 9 August 2007
Available online 16 August 2007

Abstract

The synthesis of novel *N*-acetyl-*N*,*N*-dipyrid-2-yl complexes of Rh^I and Ir^I, i.e. [RhCl(CH_3CONPy_2)(COD)] (**1**) and [IrCl(CH_3CONPy_2)(COD)] (**2**), respectively, is described. Upon prolonged treatment in CH_2Cl_2 at room temperature, complex **1** is transformed into a cationic Rh-complex, i.e. [Rh(CH_3CONPy_2)(COD)$^+$$RhCl_2(COD)^-$] (**1a**). Compound **1a** crystallizes in the monoclinic space group $P2_1/c$, complex **2** crystallizes in the triclinic space group $P\bar{1}$. Compound **1** was investigated for its catalytic activity in the hydroformylation of cyclooctene as well as of 1-octene. In addition, **1** was used in various carbonyl hydrosilylation reactions of both aldehydes and ketones. There, turn-over numbers up to 50 000 and yields in the range of 85–100% were observed. Finally, compound **1** was successfully used for the polymerization of $N_2CHCOOEt$ yielding highly stereoregular poly(ethoxycarbonylcarbene) with $M_w = 67\,000$ g/mol and a polydispersity index (PDI) of 2.59.

Keywords: Rhodium; Iridium; Hydroformylation; Carbonyl hydrosilylation; Polymerization; Diazo compounds

1. Introduction

In contrast to their P-analogues, N-based ligands are usually less strong electron donating ligands, however, possess the great advantage of being entirely stable towards oxygen even at higher temperatures. Some time ago, we reported on various dipyridylamide ligands, the corresponding Pd complexes, their immobilization on both organic and inorganic supports and their use in C–C coupling reactions such as Heck-, Suzuki and Sonogashira-Hagihara-type reactions [1–4]. Particularly Pd(II) complexes of *N*-acyl-*N*,*N*-dipyrid-2-yl amine allowed for the highly effective coupling of aryl iodides, arylbromides as well as activated aryl chlorides. Due to the high affinity of the ligand versus Pd, metal bleeding was low, allowing for the multiple use of particularly supported systems [1]. Later, non-acylated versions of dipyrid-2-ylamine were used by other groups [5–7]. In extension to our work, we report here on the synthesis of the corresponding Rh^I and Ir^I complexes of *N*,*N*-dipyrid-2-ylacetamide and their use in various catalytic reactions.

2. Results and discussion

2.1. Synthesis of Rh- and Ir-complexes of N,N-dipyrid-2-ylacetamide

Compound **1** was synthesized from $[RhCl(COD)]_2$ and *N*,*N*-dipyrid-2-ylacetamide in 95% yield (Scheme 1). Inter-

* Corresponding author. Address: Leibniz-Institut für Oberflächenmodifizierung e.V. (IOM), Permoserstraße 15, D-04318 Leipzig, Germany. Tel.: +49 (0) 341 235 2229; fax: +49 (0) 341 235 2584.
E-mail address: michael.buchmeiser@iom-leipzig.de (M.R. Buchmeiser).

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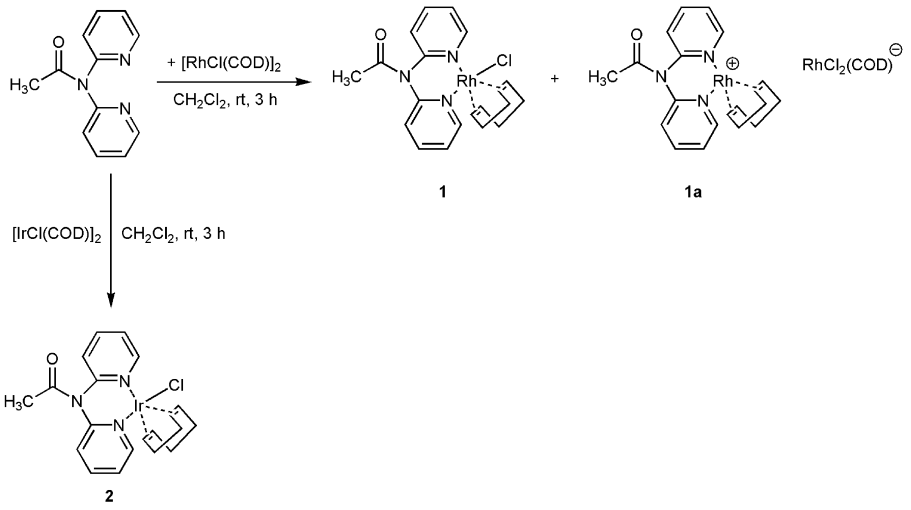
doi:10.1016/j.jorganchem.2007.08.009



Scheme 1. Synthesis of compounds **1**, **1a** and **2**.

estingly, prolonged treatment with methylene chloride gave raise to a further transformation that resulted in the formation of a cationic complex $[Rh(CH_3CONPy_2)^+RhCl_2(COD)^-]$ (**1a**). Compound **1a** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 1069.22(2)$ pm, $b = 1268.89(2)$ pm, $c = 2260.67(3)$ pm, $\alpha = \gamma = 90°$, $\beta = 95.928(1)°$, $Z = 4$ (Fig. 1a). Selected bond distances are also summarized in Fig. 1a. As can be deduced therefrom, the Rh(1)–N(1) and Rh(1)–N(2) distances were basically identical, i.e. 213.01(2) and 213.03(2) pm, the angle N(1)–Rh(1)–N(2) was 83.58(7)°.

Compound **2** was prepared in a similar manner from $[IrCl(COD)]_2$ and *N*,*N*-dipyrid-2-ylacetamide in 90% yield (Scheme 1). Compound **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 1113.34(5)$ pm, $b = 1304.17(7)$ pm, $c = 1430.73(6)$ pm, $\alpha = 96.321(2)°$, $\beta = 92.704(3)°$ and $\gamma = 105.319(2)°$, $Z = 4$ (Fig. 1b). Selected bond distances are also summarized in Fig. 1b. Surprisingly, the distances Ir–N(2) and Ir–N(3) were comparable to those found in **1a**, i.e. 212.6(6) and 213.4(6) pm, respectively. The same accounts for the angle N(2)–Ir(1)–N(3), which was 83.7(2)°. This is remarkable, since the larger atom diameter of Ir would let expect both longer bonds and a larger angle. Since the Rh-complexes are in general more reactive than the corresponding Ir-analogues, complex **1** was used for all further investigations.

2.2. Hydroformylation reactions

Hydroformylation reactions are among the most important industrial processes with a world wide production of several million tons. Starting from readily available alkenes, dihydrogen and carbon monoxide, highly valuable *n*-aldehydes as well as the corresponding regioisomers are available [8–12]. Numerous transition metals such as Rh, Pt, Co and Ru may be used for these purposes, however,

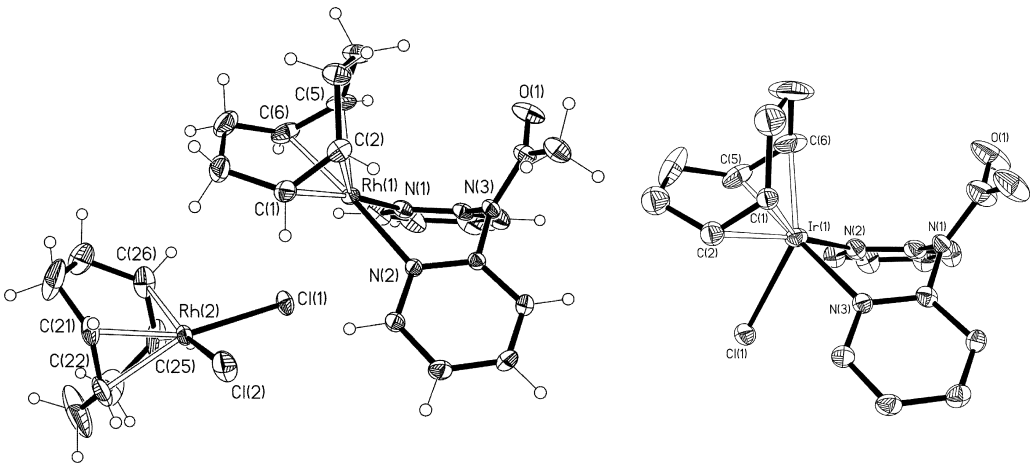


Fig. 1. X-ray structures of **1a** (left) Rh(1)–C(5) 210.1(2) pm, Rh(1)–C(6) 211.5(2) pm, Rh(1)–C(1) 212.5(2) pm, Rh(1)–N(2) 213.01(2) pm, Rh(1)–N(1) 213.05(2) pm, Rh(1)–C(2) 213.8(2) pm, Rh(2)–C(26) 208.9(3) pm, Rh(2)–C(25) 209.4(3) pm, Rh(2)–C(21) 209.9(2) pm, Rh(2)–C(22) 209.9(3) pm, N(2)–Rh(1)–N(1) 83.58(7)° and **2** (right) Ir(1)–C(5) 207.0(8) pm, Ir(1)–C(6) 209.2(9) pm, Ir(1)–N(2) 212.6(6) pm, Ir(1)–N(3) 213.4(6) pm, Ir(1)–C(1) 214.4(2) pm, Ir(1)–C(2) 218.3(2) pm, Ir(1)–Cl(1) 253.91(2) pm, N(2)–Ir(1)–N(3) 83.7(2)°.

Rh-based catalysts work at lower temperatures and are therefore often the preferred systems [13,14]. Usually, phosphane-based ligands are used, since they offer access to highly active systems and allow regio-, and in case of chiral phosphanes, even enantioselective reactions [15–24]. During the last two decades, environmental aspects including catalysts and solvent recycling became an issue. Therefore, supported [25–32], water soluble [33] or biphasic systems [34–36], as realized in the Rhone–Poulenc process, have been developed [37–40]. Alternatively, the use of ionic liquids [41–45] or supercritical CO_2 has been reported [46]. Since phosphanes and CO show similar binding constants for rhodium and high CO pressures are applied during hydroformylation, an excess of phosphane is required in order to generate a sterically demanding environment around the metal center, a prerequisite for high selectivities. In order to determine the scopes and limits of the dipyridyl amide system, we were interested, whether the corresponding Rh-complex **1** was in principle suited for this type of reaction.

For this purpose, compound **1** was used in the hydroformylation of both cyclooctene and 1-octene. Solutions of **1** and the corresponding olefin in toluene were treated with CO and H_2 (1:1) at 50 bar at 100 and 70 °C, respectively. It is worth notifying that **1** does not rearrange into **1a** in toluene, even at elevated temperature. Cyclooctene reacts smoothly under these conditions to form cyclooctane carbaldehyde. Fig. 2 illustrates the formation of cyclooctane carbaldehyde. A total TON of 1800 was obtained after 10 h, corresponding to an average turn-over frequency of 180 h^{-1}.

In case 1-octene was subject to hydroformylation, it was isomerized to the corresponding alkenes (Fig. 3), giving raise to the formation of 1-nonanal as well as the isomeric C-9 aldehydes (Fig. 4). After 3 h, 1-octene was fully converted to the corresponding aldehydes. Due to the ongoing isomerization process of 1-octene, the *n*:*iso* ratio was time

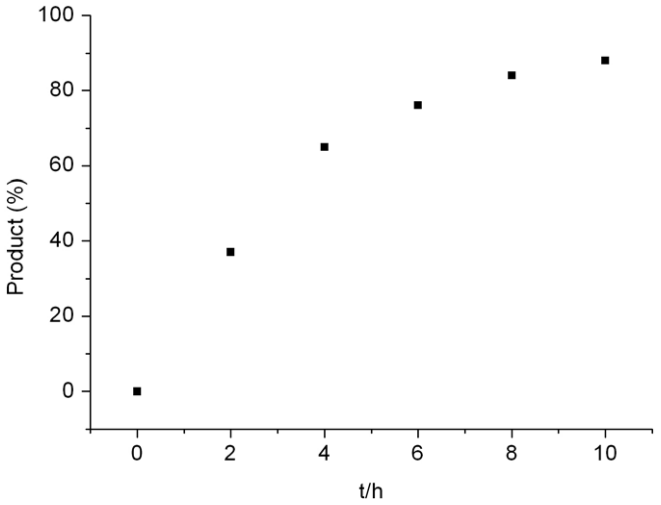


Fig. 2. Cyclooctane carbaldehyde formation from cyclooctene under hydroformylation conditions in the presence of **1**.

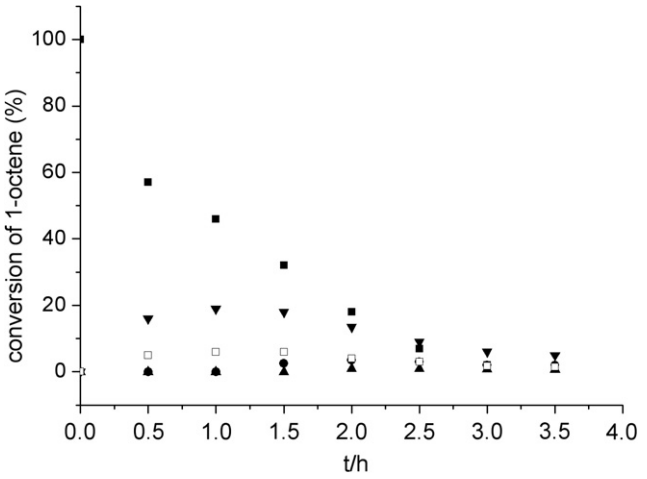


Fig. 3. Formation of isomeric octenes from 1-octene under hydroformylation conditions in the presence of **1**: s/s_0, (■) 1-octene, (▼) 2-octene. (●) 3-octene, (▲) 4-octene, (□) isomer of 1-octene.

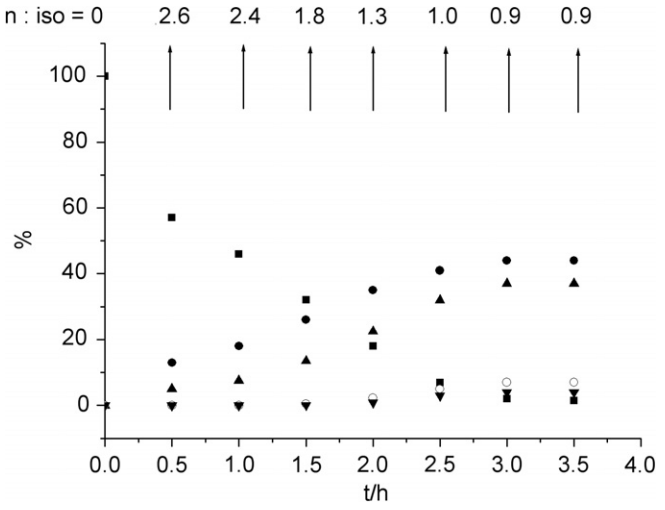


Fig. 4. Conversion (%) of 1-octene and product formation under hydroformylation conditions in the presence of **1** as well as time-dependant *n*:*iso* ration: s/s_0, (■) 1-octene, (●) nonanal, (▲) 1-methyloctanal, (○) 2-methylheptanal, (▼) 2-propylhexanal.

dependant and decreased from 2.5 to 0.8. Such a (variable, time dependant) ratio is in view of the comparably low steric demand of the ligand not surprising at all and is comparable to the one found for Rh^{I}-1,3-R_2-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = 2-Pr, mesityl), which gave raise to a final *n*:*iso* ratio of 0.9–1.4 [47]. The total TON after 4 h was found to be 4800. This corresponds to a TOF of 1200 h^{-1}. The TOF_0 was found to be 1400 h^{-1}, which is again comparable to the TOF_0 found for Rh-tetrahydropyrimidin-2-ylidenes [47] (see Fig. 5 and Scheme 2).

2.3. Carbonyl hydrosilylation reactions

Compound **1** was further used for the hydrosilylation of carbonyl compounds (Scheme 3, Table 1).

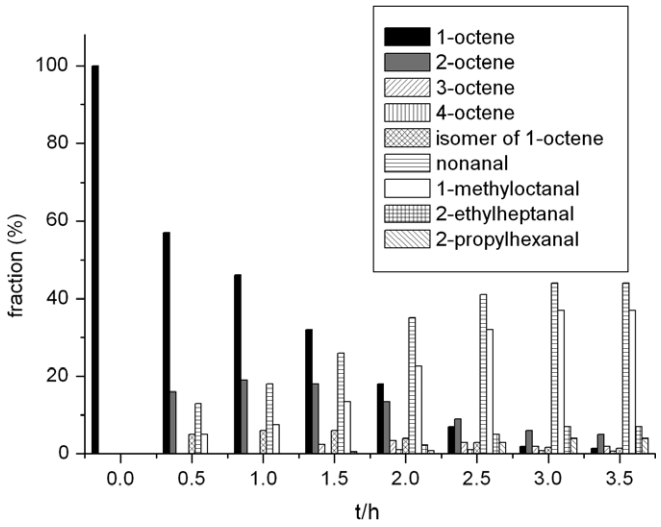
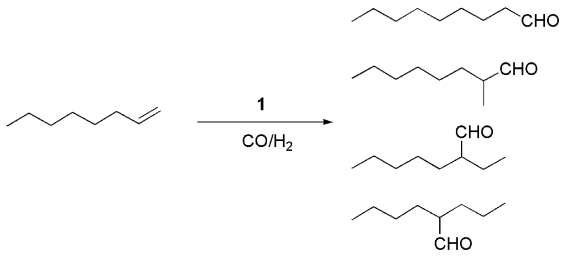
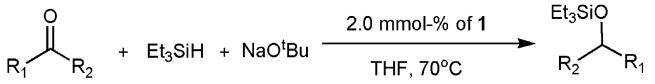


Fig. 5. Product distribution of the hydroformylation of 1-octene as a function of time using **1** as the catalyst.



Scheme 2. Hydroformylation of 1-octene by the action of **1**.



Scheme 3. Hydrosilylation of carbonyl compounds.

Table 1
Summary of carbonyl hydrosilylation results

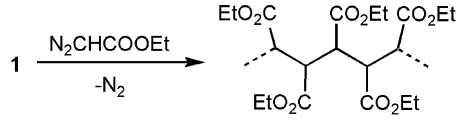
#	Substrate	*t* (h)	TON	GC yield (%)
1	Benzaldehyde	0.5	50000	100
2	4-Fluorobenzaldehyde	0.5	50000	100
3	Benzoin	1.5	42,500	85
4	*p*-*N*,*N* dimethylaminobenzaldehyde	0.5	50000	100
5	4-Chlorobenzaldehyde	1	50000	100
6	Benzophenone	1.5	48500	97
7	Benzil	4	40000	80
8	3-Hydroxybenzaldehyde	0.5	50000	100
9	3-Chloropropiophenone	1.5	44000	88

As can be deduced from Table 1, both aldehydes and ketones were successfully converted into the corresponding triethylsilyloxy compounds using low catalyst loadings, i.e. 2 mmol% (0.002 mol%) of **1**. Yields for aldehydes as determined by GC–MS were virtually quantitative, translating into turn-over numbers (TONs) of 50000. Yields for ketones were in the range of 85–97%, translating into turn-over numbers (TONs) of 42500–48500. The results obtained here are comparable to those obtained with Cu(I) complexes of 1,3-di(2-propyl)3,4,5,6-tetrahydropyrimidin-2-ylidene and 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene [48] (see Scheme 4).

2.4. Polymerization of ethyl diazaacetate

The polymerization of diazo compounds by various Rh^I complexes has attracted significant interest since it provides an attractive access to "substituted poly(methylene)" [49,50], the more as these polymerization may be carried out in a stereoselective way. Polymerization of ethyl diazoacetate using **1** yielded poly(ethyloxycarbonylcarbene) with an M_w of 67000 g/mol and a polydispersity index (PDI) of 2.59. As also reported by de Bruin, the corresponding Ir-complex **2** does not promote the polymerization of ethyl diazoacetate. Similarly, reaction of **1** with trimethylsilyldiazoacetate does not result in the formation of isolable amounts of polymer. As observed for other Rh-catalysts [49,50], the polymerization of ethyl diazoacetate by **1** does not proceed in a living or even controlled manner as is evidenced by the low yields and the higher PDI value. In addition, there is no correlation between amount of the catalyst and monomer with the molecular weight. Instead, maintaining a low concentration of monomer appears to be a crucial point in polymer synthesis. To our great pleasure, both the ^1H and ^{13}C NMR of the polymer (Fig. 6) are identical with the ones obtained by de Bruin [49,50], thus indicating the formation of a highly stereoregular, presumably syndiotactic polymer.

This finding and the absence of any chiral center in the ligand strongly supports the chain end control mechanism proposed by de Bruin [49,50].



Scheme 4. Polymerization of $N_2CHCOOC_2H_5$ by the action of **1**.

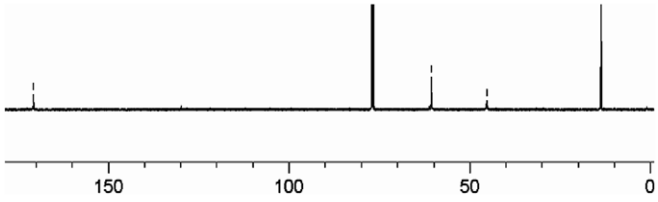


Fig. 6. ^{13}C NMR of poly(ethyloxycarbonylcarbene).

3. Experimental

3.1. General

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Triethylsilane was dried over molecular sieves and distilled under argon. Tetrahydrofurane (THF), dichloromethane and toluene were dried and purified by an MBraun SPS drying system. Cyclooctene and 1-octene were dried over CaH_2 and distilled under argon. NMR data were obtained at 250.13 MHz for proton and 62.90 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane. IR spectra were recorded on a Bruker Vector 22 using ATR technology.

3.2. Synthesis of N,N-dipyrid-2-yl acetamide (modified procedure)

The compound was prepared via a modified literature procedure [1]. In a 250 mL two neck round bottomed flask, *N*,*N*-dipyridylamine (2.0 g, 11.7 mmol), triethylamine (1.30 g, 12.8 mmol) were dissolved in 15 mL of dichloromethane. To this mixture, at −20 °C, acetyl chloride (1.70 g, 21.8 mmol), dissolved in 10 mL of dichloromethane, was added dropwise. After addition was completed, stirring was continued for a few more minutes, then the reaction mixture was warmed to room temperature. The reaction mixture was poured on saturated sodium bicarbonate solution and twice extracted with dichloromethane. The combined organic fractions were dried over Na_2SO_4, the solution was filtered and the solvent was removed *in vacuo*. The crude product mixture was passed over a short silica gel column using dichloromethane:diethyl ether (4:96 by vol.) as the mobile phase. The product was recrystallized from dichloromethane/*n*-pentane, yielding 1.7 g (68%) of **1**. Spectroscopic data were in accordance with those reported [1].

3.3. N-acetyl-N,N-dipyrid-2-yl (cyclooctadiene) rhodium chloride

N,*N*-dipyrid-2-yl acetamide (70 mg, 0.33 mmol) was dissolved in dichloromethane. This solution was added dropwise to a solution of $[Rh(COD)_2Cl]_2$ (81.5 mg, 0.165 mmol) in dichloromethane. The mixture was stirred for 3 h at room temperature, then it was filtered through glass fiber filter paper and the solvent was removed *in vacuo*. Analytically pure product was obtained as a yellow colored solid in 95% yield (143.0 mg). Crystals suitable for X-ray analysis were obtained from acetonitrile:diethyl ether ^{1}H NMR ($CDCl_3$): $\delta = 1.72$ (m, 4H of COD-CH_2), 2.15 (s, CH_3), 2.5 (m, 4H of COD-CH_2), 4.2 (s, 2H, COD-CH), 7.22, 7.5, 7.78, 8.48 (8H of Py). ^{13}C NMR ($CDCl_3$): $\delta = 24.5$, 30.97, 78.4, 122.5 (br), 138.5, 149.3, 170.7 (CO); FT-IR (ATR mode): $\bar{\nu} = 1688$ ($\upsilon_{C=O}$), 1597 (m), 1461 (s), 1431 (s), 1364 (s), 1271 (br), 992 (br), 759 cm^{-1} (m). Elemental Anal. Calc. for $C_{20}H_{23}ClN_3ORh$: C, 52.25; H, 5.04; N, 9.14. Found: C, 52.0; H, 5.15; N, 9.15%. MS (ESI) *m*/*z* calc. for $C_{22}H_{29}ClN_3ORh$: 459.06. Found: 424.09 (M^+-Cl).

3.4. Conversion of **1** into $[Rh(CH_3CONPy_2)(COD)^+RhCl_2(COD)^-]$ (**1a**)

1 was dissolved in methylene chloride and stored at −36 °C for several days. A precipitate formed that could not be dissolved in methylene chloride again. Recrystallization from acetonitrile:diethyl ether yielded orange crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$): $\delta = 1.72$ (m, br, 8H of COD-CH_2), 2.23 (br, CH_3), 2.47 (m, br, 8H of COD-CH_2), 4.14 (s, br, 4H, COD-CH), 7.27, 7.58, 7.81, 8.57 (8H of Py). ^{13}C NMR ($CDCl_3$): $\delta = 24.18$, 30.97 (br), 78.35 (br), 78.54 (br), 123.22 (br), 137.77, 150.25, 170.62 (CO); FT-IR (ATR mode): $\bar{\nu} = 2914$ (br), 1694 ($\upsilon_{C=O}$, m), 1598 (m), 1461 (m), 1365 (m), 1272 (br), 992 (br), 955 (br), 726 cm^{-1} (m).

3.5. N-acetyl-N,N-dipyrid-2-yl (cyclooctadiene) iridium chloride

N,*N*-dipyrid-2-yl acetamide (70.0 mg, 0.3286 mmol) was dissolved in dichloromethane. This solution was added dropwise to one of $[Ir(COD)Cl]_2$ (110.0 mg, 0.165 mmol) in dichloromethane (5 mL). The mixture was stirred for 3 h at room temperature and then filtered through glass fiber paper. The solvent was removed *in vacuo* and the product was obtained in pure form as a red colored solid. Crystals suitable for X-ray analysis were grown from CH_2Cl_2: diethyl ether. Yield: 162.0 mg (90.0%). ^{1}H NMR ($CDCl_3$): $\delta = 1.49$ (br, 4H of COD-CH_2), 2.23 (s, 7H, 4H of COD-CH_2 and 3H of CH_3), 3.32 (br, 4H of COD), 7.34, 7.59, 7.85, 8.74 (m, 8H of Py). ^{13}C NMR ($CDCl_3$): $\delta = 22.68$, 31.98 (br), 57.02, 122.13, 124.02, 126.01, 138.24, 139.11, 149.13, 150.56, 152.48, 169.60 (CO); FT-IR (ATR mode): $\bar{\nu} = 1695$ ($\upsilon_{C=O}$), 1461 (s), 1432(s), 1320(s), 1268 (s) cm^{-1}.

3.6. Hydroformylation reactions

The reaction was carried out in a 300 mL Parr high-pressure reactor. The reactor was evacuated, flushed with argon and filled with the rhodium complex (**1**) 10^{-5} mol, toluene (20 mL), 1-octene and cyclooctene, respectively (1.0 g, 0.009 mol), leading to a substrate to catalyst ratio of 5000:1, then *tert*-butylbenzene was added as internal standard. The mixture was pressurized with a 1:1 mixture of CO and H_2 up to a pressure of 30 bar to clean all supplies before the pressure was adjusted to 50 bar with a back pressure regulator. Samples were taken every 30 min and products were quantified by gas chromatography. The temperature was set to 100 °C for the hydroformylation of

cyclooctene and to 70 °C for the hydroformylation of 1-octene. Molar ratios of cyclooctene:**1** and 1-octene:**1** of 2000 and 5000, respectively, were used. Cyclooctene, the isomeric octenes as well as the isomeric aldehydes very identified by their MS spectra as well as by their retention times using commercially available compounds as reference material. Quantification was accomplished using *tert*-butylbenzene as an internal standard.

3.7. Typical procedure for hydrosilylation reactions

In a 50 mL Schlenk tube the catalyst (4.4 mg, 2.0 mmol%) was dissolved in 1.0 mL of THF, sodium *tert*-butoxide (4.5 mg, 10 mmol%) and 3.0 mol equivalents of triethylsilane (164 mg, 1.42 mmol) were added and the solution was stirred for 5 min. Then a solution of benzaldehyde (50 mg, 0.47 mmol) in 2.0 mL of THF was added to the reaction mixture. The solution was heated to 70 °C. Product conversion was monitored by GC–MS at defined time intervals. Compounds were identified by GC–MS. Quantification was accomplished using *tert*-butylbenzene as an internal standard.

3.8. Polymerization of diazo compounds

16.0 mg (2.0 mmol%) of the catalyst were dissolved in 2.0 mL of 1,2 dichloroethane. Ethyl diazoacetate (200.0 mg, 1.76 mmol) was dissolved in 3.0 mL of 1,2 dichloroethane. This solution was added slowly drop wise to the catalyst solution. The reaction mixture was stirred for 4 h at 65 °C, after the reaction the solvent was removed *in vacuo* and the residue was recrystallized from dichloromethane and pentane. Yield 25.0%.

3.9. Poly(ethyloxycarbonylmethylene)

FT-IR (ATR mode): $\bar{\nu} = 2980$ (br), 1724 (CO, s), 1153 (m), 1026 (m), 859 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.22 (broad t, 3H of CH_3), 3.15 (broad s, 1H, CH), 4.06 (broad, 2H of CH_2); ^{13}C NMR ($CDCl_3$) δ 13.96, 45.5, 60.82, 170.91 (CO). $M_n = 25\,800$ g/mol, $M_w = 67\,000$ g/mol, PDI = 2.59.

3.10. X-ray measurement and structure determination of *1a* and *2*

Data collection were performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo Kα-radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [51]. Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97 [52]. All non-hydrogen atoms were refined with anisotropic displacement parameters for **1a** and for most of the non-hydrogen atoms of **2**. In the asymmetric unit of **2** are two independent molecules, both showing a 1:1 position disorder of the COD molecule with partial overlying positions at the first and separate positions at the second molecule. Because of the nearly overlying positions of these COD molecules, most of the carbon atoms were refined with isotropic displacement parameters. Positions of hydrogen atoms were calculated except for those at the double bonds of the COD molecules of **1a**, which were found and refined normal with isotropic displacement parameters.

Acknowledgements

Our work was supported by a Grant of the *Deutsche Forschungsgemeinschaft* (DFG) and by the *Freistaat Sachsen*.

Appendix A. Supplementary material

CCDC 649693 and 649694 contain the supplementary crystallographic data for **1a** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.009.

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