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Note

Side chain functionalized η^5-tetramethyl cyclopentadienyl complexes of Rh and Ir with a pendant primary amine group

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ABSTRACT

Conversion of 2-(2,3,4,5-tetramethylcyclopentadien)ethylamine tautomere $C_5Me_4H_2(CHCH_2)NH_2$ (**1**) with $MCl_3 \cdot n\ H_2O$ (M = Rh, Ir) under acidic conditions gives the respective μ-chloro-bridged chelates $[(\eta^5\text{-}Me_4Cp(CH_2)_2NH_3)RhCl_2]_2Cl_2$ (**2**) and $[(\eta^5\text{-}Me_4Cp(CH_2)_2NH_3)IrCl_2]_2Cl_2$ (**3**). The dimeric complexes are received as ammonium salts and thus display good solubility in strong donor solvents such as water and DMSO. Addition of triphenyl phosphine converts Rh-dimer **2** into the mononuclear phosphine complex **4**. Under basic conditions, no intramolecular coordination of the pendant NH_2 is observed and thus the primary amino group of **4** reacts selectively with succinic anhydride by formation of a peptide bond. Hence, the electrophilic metal center and the latent nucleophilic nitrogen, which represent complementary functionalities, can be addressed separately under the appropriate reaction conditions.

1. Introduction

Half sandwich complexes of the late transition metals have become ubiquitous in organometallic chemistry [1]. Among the many developments, side chain functionalization particularly has added new facets to the chemistry of this class of compounds [2–4]. The emerging reactivity patterns have been utilized to tailor solubility [4,5], control the electronic properties of the metal center via hemi-labile coordination [5–8], introduce chirality [9], or to accelerate catalytic reactions with bifunctional mechanism [10]. Compounds with pendant amino groups have attracted considerable attention, with (2-dimethylamino)ethyl tethered η^5-cyclopentadienyl derivatives of Ru, Rh, or Ir being prominent examples [4,10]. A field of growing interest has become the conjugation of late transition metal complexes comprising appropriate functional groups with biological and bioactive compounds such as hormones [11], vitamins [12,13], peptides [14], enzymes [15] or DNA [16]. A common conjugation reaction utilizes primary amine and carboxylic acid groups to form a peptide bond. While a broad range of functionalized sandwich complexes exist [17], half sandwich complexes of late transition metals bearing carboxy functionalized side chains [18–20] or primary amine derivatives are particularly rare [20,21]. Hence, we became interested in the synthesis of late transition metal cyclopentadienyl complexes exhibiting a primary amine tether. The few examples existing for group 9 metals have been made via salt metathesis of Cp(R)Na and a M(I)X precursor. The elegant synthesis described for $[Cp^*MCl_2]_2$ (M = Rh, Ir) [22] has to date not been applied with Cp-ligands possessing a side chain amine-functionality. This may be attributed to the tedious synthetic access to such ligands [23].

We here report a synthetic route to respective rhodium(III) and iridium(III) compounds, starting from a Cp^* tautomere. Further, investigations on the selective derivatization of the side chain's functionality are presented.

2. Results and discussion

The aminoethyl-functionalized Cp^* tautomere **1** can conveniently be prepared by the published reaction sequence and thus was chosen as the bifunctional ligand in our study [24]. Formation of the Cp-π-system necessitates isomerization of the exocyclic double bond, which represents a well known reactivity of group 9 metals [25]. Primary amine moieties are known to coordinate strongly to *Lewis*-acidic transition metal centers like Rh(III) and Ir(III), which could hamper the formation of desired products. Application of acidic reaction conditions can be used to protonate the amine nitrogen and prevent metal coordination. Therefore, bifunctional ligand **1** was converted into its ammonium chloride salt prior to addition of the rhodium(III)chloride hydrate. Refluxing the reaction mixture for four days in ethanol lead to clean formation of complex **2**, which precipitates in high purity as orange powder (Scheme 1). The product can be stored under air for months without detectable decomposition. It exhibits significant solubility only in strong donor solvents like water or DMSO, which are

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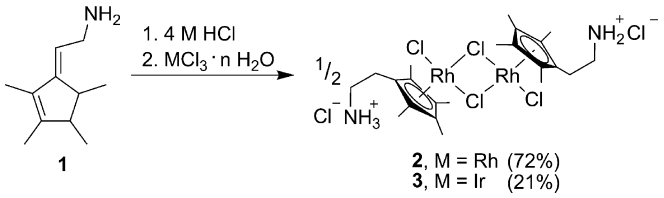
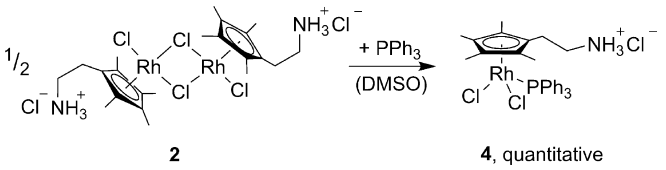


Scheme 1. Synthesis of dinuclear μ-chloro bridged group 9 metal complexes **2** and **3**.



Scheme 2. Donor induced splitting of dinuclear complex **3**.

capable of metal coordination and splitting of the dimeric structure [6,26].

Synthesis of the homolog iridium complex **3** reveals distinct reactivity differences of the two group 9 metals, which are less pronounced for the synthesis of the μ-chloro bridged η^5-cyclopentadienyl analogues $[Cp^*MCl_2]_2$ (M = Rh, Ir) under similar conditions [22], yet have been reported to strongly influence synthesis of $[Cp^*MCl_2]_2$ from hexamethyl dewar benzene [27]. In contrast to rhodium complex **2**, iridium cyclopentadiene derivative **3** remains dissolved. The markedly increased solubility of complex **3** seems to limit product formation to equilibrium concentration and no additional conversion is observed after 24 h. The product was obtained upon removal of solvent and washing with non polar solvents in high purity as bright yellow powder.

^{1}H NMR spectra of complex **2** and **3** in DMSO-d_6 are nearly identical. Good solubility and comparison with literature data support the assumed monomeric structure with one donor solvent coordinated to the metal center [28], however formation of an internal salt of the composition $[(\eta^5\text{-}Me_4Cp(CH_2)_2NH_3)RhCl_3]$ as well as other fast chloride dissociation equilibria can not be ruled out completely. The NH_3^+ group gives rise to a broad singlet at δ = 8.10 (**2**) or δ = 8.12 (**3**) which integrates to three protons, indicating, that the amine tether does not coordinate to the metal center. Hence, hemi-lability of the amino side chain may be controlled by protonation/deprotonation, which contrasts the properties of other hemilabile moieties, e.g. alkenyl functionalities which have been know for several decades.[8] Resonances observed for the methyl (two singlets centered at δ = 1.7 ppm) and methylen (triplets at about δ = 2.9 and δ = 2.4 ppm) moieties are in agreement with those observed for similar compounds. [6] The methylene resonances were assigned based on ^{1}H,^{1}H COSY spectra. The strong downfield shift of the methylene protons adjacent to the nitrogen is also indicative for a protonation of the amino function [5,7].

^{13}C NMR reveals η^5-coordination of the cyclopentadiene system in complexes **2** and **3**, since chemical shifts are in the typical range [6]. For complex **2**, carbon resonances are split into doublets due to a $^1J_{Rh,C}$ coupling, with coupling constants ranging from 8.1 Hz to 7.3 Hz, which is close to literature data for $[Cp^*RhCl_2PPh_3]$ ($^1J_{Rh,C}$ = 6.2 Hz) [27,29]. While for both complexes the chemical shifts of the methyl and methylene resonances are very similar, evaluation of ^{13}C NMR spectra reveals clear differences for the cyclopentadienyl signals. In comparison to Rh complex **2** (102.6, 94.0, 93.8), resonances for Ir compound **3** (97.1, 92.2, 85.8) are shifted upfield by 6-8 ppm and cover a broader frequency range (**2**: 8.9 ppm, **3**: 11.3 ppm, see Fig. 1). This indicates a lower degree of π-aromatization for the Ir compound.

While bubbling CO through a DMSO-solution of complex **2** did only yield a transient band at 2066 cm^{-1}, the coordinated donor solvent was displaced irreversibly upon addition of triphenyl phosphine. Resulting complex **4** can be isolated in quantitative yields after removal of the solvent (Scheme 2). ^{31}P NMR of **4** shows a doublet at 30.3 ppm with a $^1J_{Rh,C}$ coupling constant of 144 Hz and thus is similar to that reported for $[Cp^*RhCl_2PPh_3]$ (δ = 30.6 ppm, $^1J_{Rh,C}$ = 144 Hz) [30,31]. Despite of the extra PPh_3 signals, ^{1}H NMR of complex **4** resembles the one of the precursor **2** with a broad NH_3^+ resonance at 8.18 ppm. ^{13}C NMR reveals the intact η^5-coordination of the π-ligand, with a markedly decreased spread of the Cp-carbon signals (101.3, 98.6, 98.2 ppm). These resonances are split by $^1J_{Rh,C}$ couplings, ranging from 6.8 to 5.9 Hz and additional $^2J_{P,C}$ coupling ranging from 5.9 to 1.5 Hz (Fig. 1). Further, $^3J_{P,C}$ coupling of 1.4 to 0.7 Hz is observed for Cp*-methyl groups.

According to spectroscopical data, the nitrogen atom in complexes **2**, **3** and **4** is protonated and does not coordinate to the metal center. Besides, elemental analysis is in agreement with

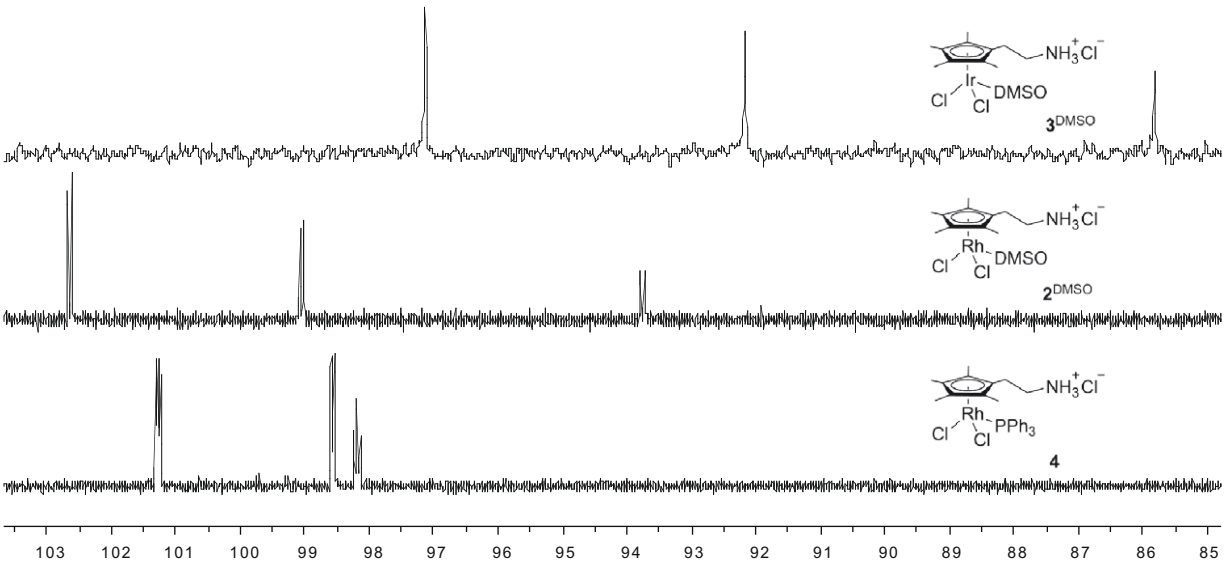
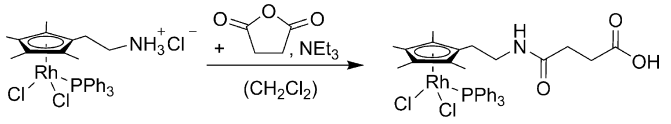


Fig. 1. Comparison of the Cp of complexes **2**, **3** and **4** (^{13}C NMR, DMSO-d_6).



Scheme 3. Side-chain selective modification of **4** with succinic anhydride.

isolation of HCl adducts. Side chain selective derivatization necessitates deprotonation of the amino group. Yet, it has been shown for similar complexes, that the nucleophilic nitrogen atom coordinates intramolecular to the electrophilic metal center. [6] In **4** however, the triphenyl phosphine prevents immediate coordination of the nucleophilic nitrogen. Correspondingly, reaction with succinic anhydride in dichloromethane under basic conditions leads to peptide bond formation, yielding pure phosphine adduct **5** after acidic workup in 54% yield (Scheme 3).

Conversion was confirmed by IR spectroscopy due to the presence of bands which can be assigned to carbonic acid ($\tilde{\nu}$(CO) = 1730 cm^{-1}) and amide ($\tilde{\nu}$(amide I) = 1647 cm^{-1}, $\tilde{\nu}$(amide II) = 1545 cm^{-1}) functionalities. The [$Cp^*Rh(PPh_3)Cl_2$] core of **5** is unaltered as judged by the minor changes in ^1H, ^{13}C, ^1H,^1H COSY and ^{31}P NMR in comparison to precursor **4**. In agreement with the IR data, ^{13}C NMR shows two carbonyl resonances at δ = 174.4 ppm and 174.7 ppm, while ^1H NMR reveals the presence of an amide proton at δ = 7.60 ppm.

3. Conclusion

Synthesis of the first example of $Cp^*Rh(III)$ and $Cp^*Ir(III)$ complexes comprising a primary amine-functionality in the side chain can be achieved under acidic reaction conditions employing ligand precursor **1**. If the coordination sphere of the d_6 cation is electronically saturated, e.g. by addition of triphenyl phosphine, side chain selective derivatization can be achieved under basic conditions. Hence metal center and side chain functionality can be addressed independently under appropriate conditions. This enables the bifunctional Cp^*-derived ligand **1** to covalently conjugate reactive late transition metal cations with functionalities of other molecules, e.g. carboxyl groups.

4. Experimental

4.1. General remarks

Elemental analyses were obtained from the Microanalytical Laboratory of Technische Universität München. Spectroscopic data were recorded on the following instruments: IR spectra: Jasco FT/IR-460 PLUS (KBR pallets); mass spectra: Thermo Electron LCQ classic. NMR spectra: BRUKER DRX 500 (^1H NMR 500.13 MHz, ^{13}C NMR 125.76 MHz, ^{31}P NMR 202.27 MHz) or JEOL JNM-GX 400 (^1H NMR 400.13 MHz, ^{13}C NMR 100.53 MHz, ^{31}P NMR 161.83 MHz), T = 300 K, calibration to the residual proton resonance and the natural abundance ^{13}C resonance of the solvent (DMSO-d_6:, δ_H = 2.50 and δ_C = 39.52 ppm; $CDCl_3$, δ_H = 7.25 and δ_C = 77.16 ppm). ^{31}P NMR chemical shifts are reported relative to external phosphoric acid (δ = 0.0 ppm). Signal multiplicities are abbreviated as: s (singlet), d (dublet), t (triplet), m (multiplet), br (broad). Commercially available solvents and reagents were purified according to literature procedures. All reactions were carried out in degassed solvents under an argon atmosphere. Succinic anhydride, rhodium(III)chloride hydrate and iridium(III)chloride hydrate were obtained from Sigma Aldrich and used without further purification. 2-(2,3,4,5-Tetramethylcyclopentadienyl)ethylamine tautomere **1** [24] and [$Cp^*Rh(PPh_3)Cl_2$] [27,28] were prepared as reported previously.

4.2. Preparation of [(η^5-$Me_4Cp(CH_2)_2NH_3$)$RhCl_2$]$_2Cl_2$ (**2**)

2-(2,3,4,5-Tetramethylcyclopentadienyl)ethylamine tautomere **1** (496 mg, 3.00 mmol) was dissolved in diethylether (10 mL) and treated with hydrochloric acid (1.47 mL, 5.9 mmol, 4 M in dioxane). Hexanes (20 mL) was added to this solution until a white precipitate formed, which was filtered off and washed twice with hexanes. The white solid was dissolved in ethanol (50 mL) and $RhCl_3 \cdot n\ H_2O$ (184 mg, 0.70 mmol) was added. The reaction mixture was refluxed for 4 days and thereafter stored at −20 °C over night. The precipitate was filtered off and washed with hexanes, diethylether and cold ethanol to yield 190 mg of the pure product (0.25 mmol; 72%) as an orange powder. ^1H NMR (DMSO-d_6): δ (ppm) = 8.10 (br s, 3H, –NH_3), 2.94 (t, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2NH_3$), 2.48 (t, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2NH_3$), 1.74/1.65 (s, 12H, CH_3). ^{13}C NMR (DMSO-d_6): δ (ppm) = 102.6 (d, $^1J_{RhC}$ = 7.3 Hz, C_{Cp}), 99.0 (d, $^1J_{RhC}$ = 7.5 Hz, C_{Cp}), 93.8 (d, $^1J_{RhC}$ = 8.1 Hz, C_{Cp}), 36.4 (s, $CH_2CH_2NH_3$), 22.0 (s, $CH_2CH_2NH_3$), 9.2/8.9 (2x s, CH_3). ESI-MS m/z (%) = 302.1 (100) [½M−Cl−HCl]$^+$, 639.0 (55) [M−Cl−2HCl]$^+$. IR [cm^{-1}] $\tilde{\nu}$ = 3114 s, 3019 m, 2920 m, 2852 w, 2360 w, 1622 s, 1464 s, 1376 m, 1262 w, 1132 m, 1024 m, 930 w, 817 w, 763 w. Anal. Calc. for $C_{22}H_{38}N_2Cl_6Rh_2$ (749.1): C, 35.27; H, 5.11; N, 3.74. Found: C, 35.01; H, 5.19; N, 3.55%.

4.3. Preparation of [(η^5-$Me_4Cp(CH_2)_2NH_3$)$IrCl_2$]$_2Cl_2$ (**3**)

2-(2,3,4,5-Tetramethylcyclopentadienyl)ethylamine tautomere **1** (100 mg, 0.60 mmol) was dissolved in diethylether (2.5 mL) and treated with hydrochloric acid (0.29 mL, 1.2 mmol, 4 M in dioxane). To this solution, hexanes (5 mL) was added until a white precipitate formed which was filtered of and washed two times with hexanes. The white solid was dissolved in dry ethanol (10 mL) and $IrCl_3 \cdot n\ H_2O$ (55.7 mg, 0.19 mmol) was added. The reaction mixture was refluxed for 16 h after which the solution was filtered. Volatiles were evaporated under reduced pressure and the residue washed with diethylether and hexanes, yielding 15.8 mg of the pure product (0.04 mmol, 21%) as a yellow powder. ^1H NMR (DMSO-d_6): δ (ppm) = 8.12 (br s, 3H, –NH_3), 2.90 (m, 2H, $CH_2CH_2NH_3$), 2.39 (t, 2H, $^3J_{HH}$ = 8.1 Hz, $CH_2CH_2NH_3$), 1.74/1.64 (s, 12H, CH_3). ^{13}C NMR (DMSO-d_6): δ (ppm) = 97.1/92.2/85.8 (C_{Cp}), 36.8 ($CH_2CH_2NH_3$), 22.1 ($CH_2CH_2NH_3$), 8.9/8.8 (CH_3). Anal. Calc. for $C_{22}H_{38}N_2Cl_6Ir_2$ (927.7): C, 28.48; H, 4.13; N, 3.02. Found: C, 28.16; H, 4.22; N, 2.96%.

4.4. [(η^5-$Me_4Cp(CH_2)_2NH_3$)$RhCl_2(PPh_3)$] (**4**)

[(η^5-$Me_4Cp(CH_2)_2NH_3$)$RhCl_2$]$_2Cl_2$ **2** (40 mg, 0.05 mmol) and triphenylphosphine (28 mg, 0.11 mmol) were dissolved in dimethylsulfoxide (1.2 mL) and vigorously stirred for 1 h. The solvent was removed under reduced pressure and the residue washed with diethylether. The product was obtained as a red powder in quantitative yield (68 mg). ^1H NMR (DMSO-d_6): δ (ppm) = 8.18 (br s, 3H, NH_3), 7.72 (m, 6 H, $C_{PPh3}H$), 7.48 (m, 9H, $C_{PPh3}H$), 2.86 (t, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2NH_3$), 2.34 (t, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH_2NH_3$), 1.38 (d, 6H, $^4J_{PH}$ = 3.1 Hz, CH_3), 1.13 (d, 6H, $^4J_{PH}$ = 2.9 Hz, CH_3). ^{13}C NMR (DMSO-d_6): δ (ppm) = 134.7 (d, J_{PC} = 9.7 Hz, C_{PPh3}), 131.0/128.4 (2x br, C_{PPh3}), 101.3 (dd, $^1J_{RhC}$ = 6.3 Hz, $^2J_{PC}$ = 2.9 Hz, C_{Cp}), 98.6 (dd, $^1J_{RhC}$ = 6.8 Hz, $^2J_{PC}$ = 1.5 Hz, C_{Cp}), 98.2 (dd, $^1J_{RhC}$ = 5.9 Hz, $^2J_{PC}$ = 5.9 Hz, Cp), 36.3 (d, $^4J_{PC}$ = 4.9 Hz, $CH_2CH_2NH_3$), 22.3 (s, $CH_2CH_2NH_3$), 8.9 (d, $^3J_{PC}$ = 1.4 Hz, CH_3), 8.7 (d, $^3J_{PC}$ = 0.7 Hz, CH_3). ^{31}P NMR (DMSO-d_6): δ (ppm) = 30.27 (d, $^1J_{P,Rh}$ = 144 Hz). ESI-MS m/z (%) = 302.1 (100) [M−PPh_3−Cl−HCl]$^+$, 564.0 (54) [M−Cl−HCl]$^+$. IR [cm^{-1}] $\tilde{\nu}$ = 2959 w, 1725 w, 1622 w, 1482 s, 1435 vs, 1384 vs,

1269 w, 1094 w, 1020 w, 745 m, 687 s, 525 s. Anal. Calc. for $C_{29}H_{34}NCl_3PRh \cdot 0.5\ Me_2SO$ (675.9): C, 53.31; H, 5.52; N, 2.07. Found: C, 52.71; H, 5.34; N, 2.03%.

4.5. [(η^5-$Me_4Cp(CH_2)_2NHCO(CH_2)_2COOH)RhCl_2(PPh_3)$] (**5**)

[(η^5-$Me_4Cp(CH_2)_2NH_3)RhCl_2PPh_3$]Cl **4** (100 mg, 0.16 mmol) was dissolved in dichloromethane (5 mL), and succinic anhydride (20 mg, 0.16 mmol) and triethylamine (440 μL, 3.2 mmol) were added. The mixture was stirred at room temperature for 24 h and subsequently washed with 0.1 M HCl and brine (each 3 × 10 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to about 20% of the original volume. Addition of hexanes led to precipitation of the product as a red powder, which was filtered off and dried *in vacuo* (60.5 mg, 0.84 mmol, 54%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.75 (m, 6H, $C_{PPh3}H$), 7.60 (m, 1H, N*H*), 7.37 (m, 9 H, $C_{PPh3}H$), 3.47 (m, 2H, CH_2CH_2NH), 2.47-2.35 (m, 4H CH_2CO), 3.46 (m, 2H, CH_2CH_2NH), 1.36 (d, 6H, $^4J_{PH}$ = 1.3 Hz, CH_3), 1.05 (d, 6H, $^4J_{PH}$ = 2.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 174.7/174.4 (2x s, *C*O), 134.8 (d, J_{PC} = 9.2 Hz, C_{PPh3}), 130.7/128.1 (2x br, C_{PPh3}), 103.2 (d, $^1J_{RhC}$ = 3.8 Hz, C_{Cp}), 101.2 (dd, $^1J_{RhC}$ = 8.5, $^2J_{PC}$ = 6.2 Hz, C_{Cp}), 96.2 (d, $^1J_{RhC}$ = 6.1 Hz, C_{Cp}), 36.4 (d, $^4J_{PC}$ = 4.6 Hz, CH_2CH_2NH), 31.0/30.4 (2x s, *C*H_2CO), 24.7 (s, *C*$H_2CH_2NH_3$), 9.7/8.7 (2x s, *C*H_3). ^{31}P NMR ($CDCl_3$): δ (ppm) = 30.07 (d, $^1J_{RhP}$ = 143 Hz). ESI-MS *m*/*z* (%) = 366.0 (100) [M−PPh_3−Cl−HCl]$^+$, 402.0 (75) [M−PPh_3−Cl]$^+$, 663.9 (42) [M−Cl]$^+$. IR [cm^{-1}] $\tilde{\nu}$ = 3057 m, 2957 sh, 2925 m, 1730 m, 1647 s, 1545 m, 1483 m, 1435 vs, 1384 vs, 1095 m, 1022 w, 748 m, 698 s, 525 s. Anal. Calc. for $C_{33}H_{37}NCl_2O_3PRh \cdot H_2O$ (718.5): C, 55.17; H, 5.47; N, 1.95. Found: C, 54.93; H, 5.68; N 1.95%.

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References

[1] (a) P. Jutzi, U. Siemeling, J. Organomet. Chem. 500 (1995) 175;
(b) C. Janiak, H. Schumann, Adv. Organomet. Chem. 33 (1991) 291;
(c) N.J. Coville, K.E. du Plooy, W. Pickl, Coord. Chem. Rev. 20 (1992) 116.
[2] P. Jutzi, J. Dahlhaus, Synthesis (1993) 684.
[3] (a) P. Jutzi, J. Dahlhaus, M.O. Kristen, J. Organomet. Chem. 450 (1993) C1–C3;
(b) P. Jutzi, J. Dahlhaus, M.J. Bangel, J. Organomet. Chem. 460 (1993) C13–C15.
[4] C. Müller, V. Derk, P. Jutzi, J. Organomet. Chem. 600 (2000) 127.
[5] (a) A.I. Philippopooulos, N. Hadjiliadis, C.E. Hart, B. Donnadieu, P.C. McGowan, R. Poilblanc, Inorg. Chem. 36 (1997) 1842;
(b) P.C. McGowan, C.E. Hart, B. Donnadieu, R. Poilblanc, J. Organomet. Chem. 528 (1997) 191;
(c) P.K. Chan, W.K. Leong, K.I. Krummel, M.V. Garland, Eur. J. Inorg. Chem. (2006) 1568.
[6] P. Jutzi, M.O. Kristen, B. Neumann, H.-G. Stammler, Organometallics 13 (1994) 3854.
[7] (a) A.I. Philippopoulos, B. Donnadieu, R. Poilblanc, N. Hadjiliadis, J. Organomet. Chem. 582 (1999) 286;
(b) A.I. Philippopoulos, R. Poilblanc, N. Hadjiliadis, Inorg. Chim. Acta 283 (1998) 24.
[8] (a) For examples of functionalized Cp ligands showing a hemi-labile coordinating alkenyl side-chains see: J. Okuda, K.H. Zimmermann, Chem. Ber. 122 (1989) 1645;
(b) J. Okuda, K.H. Zimmermann, Angew. Chem. Int. Ed. 30 (1991) 430;
(c) K.H. Zimmermann, R.S. Pilato, I.T. Horváth, J. Okuda, Organometallics 11 (1992) 3935.
[9] F.K. Cheung, C. Lin, F. Minissi, A.L. Crivillé, M.A. Graham, D.J. Fox, M. Wills, Org. Lett. 9 (2007) 4659.
[10] (a) J.A. Ayllon, S.F. Sayers, S. Sabo-Etienne, B. Donnadieu, B. Chaudret, E. Clot, Organometallics 18 (1999) 3981;
(b) T. Matsubara, K. Hirao, Organometallics 20 (2001) 5759;
(c) Y.F. Lam, C.Q. Yin, C.H. Yeung, S.M. Ng, G. Jia, C.P. Lau, Organometallics 21 (2002) 1898;
(d) C. Fuquiang, Organometallics 25 (2006) 4034.
[11] (a) M. Cais, E. Slovin, L. Snarsky, J. Organomet. Chem. 160 (1978) 223;
(b) B. Ferber, S. Top, A. Vessières, R. Welter, G. Jaouen, Organometallics 25 (2006) 5730.
[12] M.E. Wilson, G.M. Whitesides, J. Am. Chem. Soc. 100 (1978) 306.
[13] (a) G. Klein, N. Humbert, J. Gradinaru, A. Ivanova, F. Gilardoni, U.E. Rusbandi, T.R. Ward, Angew. Chem. Int. Ed. 44 (2005) 7764;
(b) M. Creus, T.R. Ward, Org. Biomol. Chem. 5 (2007) 1835.
[14] J. Lemke, N. Metzer-Nolte, Eur. J. Inorg. Chem. (2008) 3359.
[15] P. Haquette, B. Talbi, S. Canaguier, S. Dagorne, C. Fosse, A. Martel, G. Jaouen, M. Salmain, Tetrahedron Lett. 49 (2008) 4670.
[16] W.A. Wlassoff, G.C. King, Nucleic Acids Res. 30 (2002) e58.
[17] (a) For reviews see: G. Jaouen, A. Vessières, I.S. Butler, Acc. Chem. Res. 26 (1993) 361;
(b) K. Severin, R. Bergs, W. Beck, Angew. Chem. Int. Ed. 37 (1998) 1635;
(c) D.B. Grotjahn, Coord. Chem. Rev. 190–192 (1999) 125;
(d) R. Alberto, J. Organomet. Chem. 692 (2007) 1179.
[18] X. You-Feng, S. Yan, P. Zhen, J. Organomet. Chem. 689 (2004) 823.
[19] (a) J.A. Miguel-Garcia, P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1990) 1473;
(b) J.A. Miguel-Garcia, H. Adams, N.A. Bailey, P.M. Maitlis, J. Chem. Soc., Dalton Trans. (1992) 131;
(c) R. Stodt, S. Gencaslan, I.M. Müller, W.S. Sheldrick, Eur. J. Inorg. Chem. (2003) 1873.
[20] (a) H. Dialer, P. Mayer, K. Polborn, W. Beck, Eur. J. Inorg. Chem. (2001) 1051;
(b) H. Dialer, W. Steglich, W. Beck, Tetrahedron 57 (2001) 4855.
[21] (a) Y. Miyaki, T. Onishi, H. Kurosawa, Inorg. Chim. Acta 300 (2000) 369;
(b) C. Scolaro, T.J. Geldbach, S. Rochat, A. Dorcier, C. Gossens, A. Bergamo, M. Cocchietto, I. Tavernelli, G. Sava, U. Rothlisberger, P.J. Dyson, Organometallics 25 (2006) 756;
(c) A. Casini, C. Gabbiani, F. Sorrentino, M.P. Rigobello, A. Bindoli, T.J. Geldbach, A. Marrone, N. Re, C.G. Hartinger, P.J. Dyson, L. Messori, J. Med. Chem. 51 (2008) 6773.
[22] C. White, A. Yates, P.M. Maitlis, D.M. Heinekey, Inorg. Synth. 29 (1992) 228.
[23] (a) A. Avey, D.R. Tyler, Organometallics 11 (1992) 3856;
(b) O. Segnitz, M. Winter, K. Merz, R. Fischer, Eur. J. Inorg. Chem. (2000) 2077.
[24] D. van Leusen, D.J. Beetstra, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 4084.
[25] S. Carrà, R. Ugo, Inorg. Chim. Acta Rev. 1 (1967) 49.
[26] (a) A.I. Philippopoulos, R. Bau, R. Poilblanc, N. Hadjiliadis, Inorg. Chem. 37 (1998) 4822;
(b) E. Nakatani, Y. Takai, H. Kurosawa, J. Organomet. Chem. 692 (2007) 278–285.
[27] (a) J.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970;
(b) B.L. Booth, R.N. Haszeldine, M. Hill, J. Organomet. Chem. 16 (1969) 491.
[28] E. Alessio, Chem. Rev. 104 (2004) 4203–4242.
[29] B. Paz-Michel, M. Cervantes-Vazquez, M.A. Paz-Sandoval, Inorg. Chim. Acta 361 (2008) 3094.
[30] V. Tedesco, W. von Philipsborn, Mag. Res. Chem. 34 (1996) 373.
[31] W.D. Jones, V.L. Kuykendall, Inorg. Chem. 30 (1991) 2615.