Synthesis and aromatizational rearrangements of new imino-, hydrazono-, and azino-2,5-cyclohexadienylidene systems as ligands for cascade type metallocomplexes

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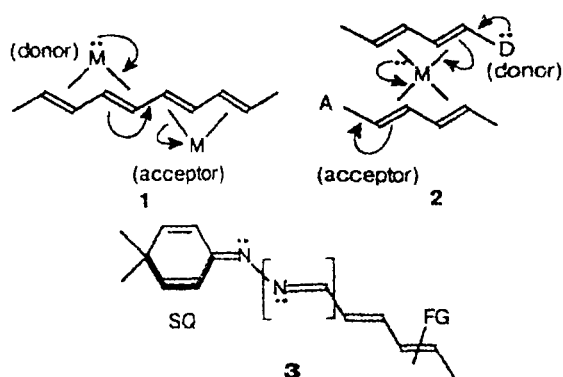Fax: 007 (095) 135 5085. E-mail: vanik@ineos.ac.ru*

Three approaches to the synthesis of *N*-substituted imino-, hydrazono-, and azino-2,5-cyclohexadienylidene systems based on reactions of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone with aminophenols and hydrazones and condensation of hydrazones of *para*-semiquinoid ketones with carbonyl compounds, including that of the ferrocene series, were realized. The latter reaction, when applied to 3,6-dibromophenanthrene-9,10-quinone, was accompanied by quantitative aromatizational molecular rearrangement with the elimination of the CCl_3 group. Using Rh^I complexes as an example, it was shown that the heteroorganic ligands obtained can be used for the synthesis of mixed-ligand metallocomplexes with triple coordination of the metal atom including simultaneous metal—ligand interactions of the n-, π-, and σ-types.

Key words: cyclohexadienones, Schiff's condensations, imines, hydrazones, azines; aromatizational rearrangement, rhodium complexes.

In the course of synthetic studies of polyheteroatomic cascade type **1** and **2*** metallocomplexes,[1—5] we focussed on the possibility of obtaining a variety of "composite" cross-multiconjugated imino-, hydrazono-, and azino-2,5-cyclohexadienylidene ligands (**3**). In these compounds, the potentially metal-coordinating *para*-semiquinoid (SQ) and other unsaturated fragments, including those containing active functional groups (FG), are bonded by the bridges of one or two trigonally hybridized nitrogen atoms.
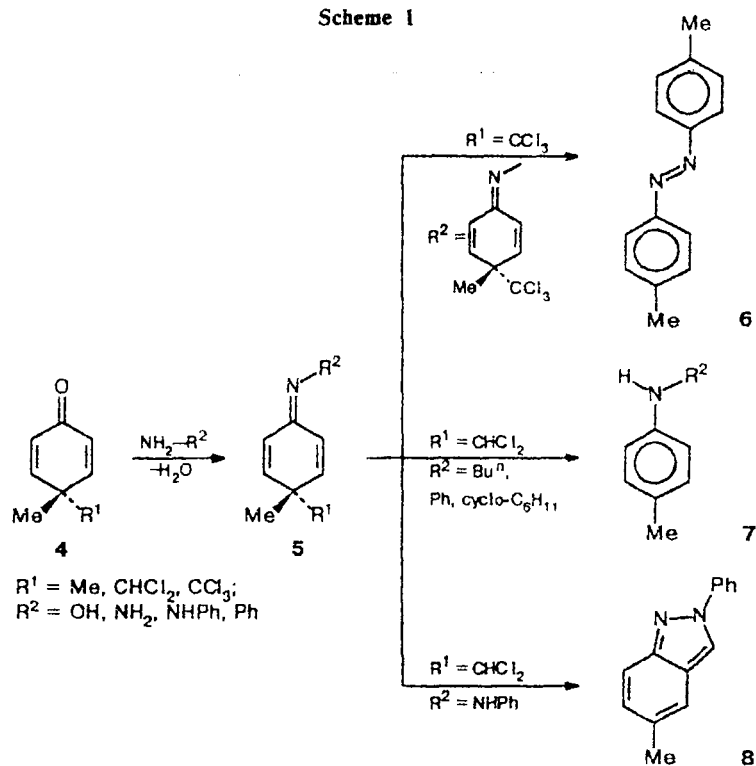
According to the literature data, the chemistry of imino derivatives with the cyclohexadienylidene structure (Scheme 1) is restricted to a series of the simplest representatives **5** obtained from 4,4-disubstituted 2,5-cyclohexadienones (**4**) (for reviews see Refs. 6, 7). Some of them undergo skeletal rearrangements with elimination (or migration) of one of the geminal substituents and the formation of products **6**, **7**, and **8** (see Refs. 8, 9—11, and 12, respectively).

(donor) M / (acceptor) **1**

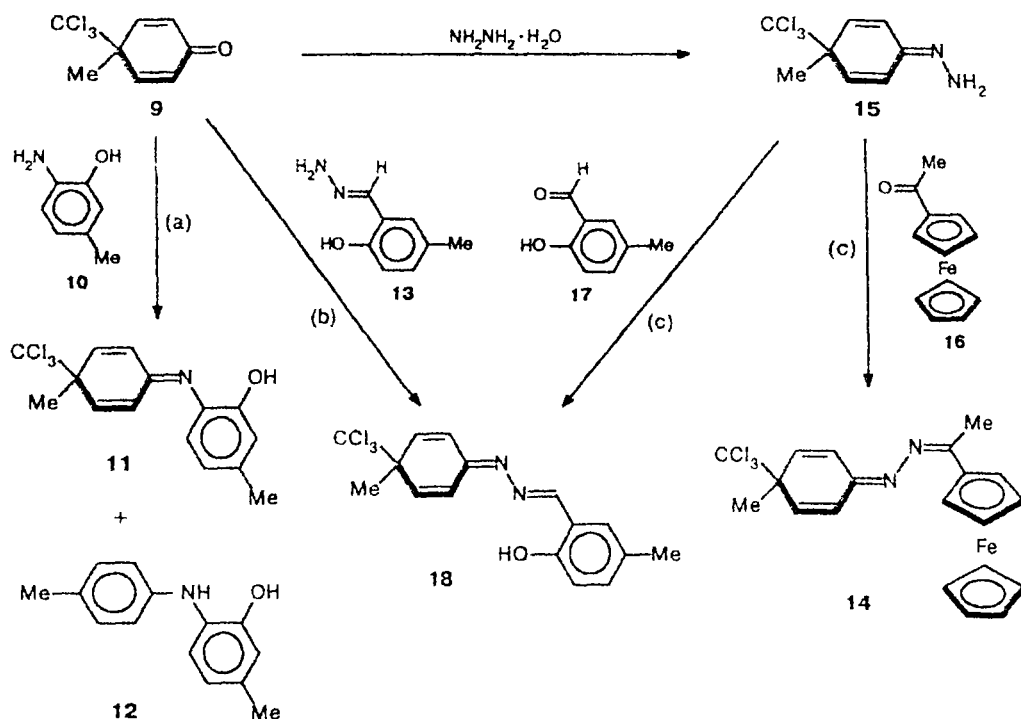(donor) / (acceptor) **2**

SQ / FG **3**

To evaluate the synthetic accessibility of new, type 3 imino-, hydrazono-, and azino-2,5-cyclohexadienylidene ligands and their stability with respect to possible aromatizational rearrangements, we studied the Schiff's condensation of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone (**9**) [13] with several functionally substituted amines. The latter could impart the additional potential for simultaneous mixed coordination of the metal atom (of the n-, π-, and σ-type) to the new "cascade" type ligands formed. In the present work, the target polyfunctional ligands were prepared by three independent synthetic routes (Scheme 2): (a) a *para*-semiquinoid fragment was coupled with the exo-functional fragment through the =N— bridge; (b) the above fragments were coupled through the azine bridge introduced from the

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* The principle of metal—ligand "cascade" appeared as a result of the generalization of two new phenomena of organometallic stereodynamics, which we have found recently[2,3] and have called oxidative and reductive redox-rotation. In the "cascade", type **1** ("metal—ligand—metal") or type **2** ("ligand—metal—ligand") metallocomplexes, one or several coordinated metal atoms capable of concertedly and reversibly changing their valence in the course of intramolecular conformational transformation are in positions of mutual conjugation.

Scheme 1

R^1 = Me, CHCl$_2$, CCl$_3$;
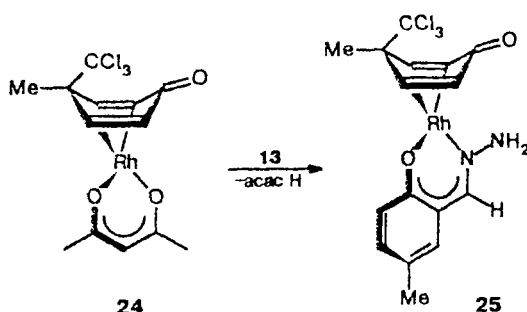R^2 = OH, NH$_2$, NHPh, Ph

Scheme 2

functional component; (c) the azine bridge was introduced to the ligand from the *para*-semiquinoid component. The first route is effected in the smooth condensation of dienone **9** with 2-amino-5-methylphenol (**10**). A new semiquinoid system **11** contains an additional, potentially metal-coordinating chelate site at the exo-

Scheme 3

position of the molecule in addition to the diene system of the ring. The possibility of skeletal molecular rearrangements associated with the transition of a molecule to a more stable aromatic form is one of the limitations in obtaining new "cascade" type ligands containing a nitrogen atom at the exo-position. In fact, along with the Schiff's base 11, amine 12 was isolated from the reaction mixture in a low yield. This compound is similar to the rearrangement products previously observed for other imino derivatives of *para*-semiquinoid systems[10,11] (*cf.* transformations 5 → 7 in Scheme 1). Condensation of dienone 9 with 5-methylsalicylaldehyde hydrazone (13) in methanol occurs with retention of its *para*-semiquinoid system and the appearance of a remote, potentially metal-coordinating chelate site (compound 18). We obtained the same compound in the reaction of 5-methylsalicylaldehyde (17) with *para*-semi-quinone hydrazone 15. The latter also readily reacts with acetylferrocene 16 to give ligand 14 with the metallocenyl moiety incorporated in the main chain of conjugation. It is of note that this compound exists in

solution at ambient temperature as one (likely, the most stable) *anti*-stereoisomer. This follows from its NMR spectrum, where only one set of signals for each of the Me groups of the molecule is present. Hydrazone 15 also readily reacts with 3,6-dibromophenanthrene-9,10-quinone (19) (Scheme 3). However, in this case, the reaction did not result in the expected azine 20, but was rather accompanied by a redox rearrangement with elimination of the trichloromethyl group and the formation of a mixture of tautomers of *para*-tolylhydrazone of the initial quinone 21. Similar products were obtained by the condensation of phenanthrene-9,10-quinone with phenylhydrazine.[14] The formation of one more product, azine 22, allows one to suggest an alternative intermolecular redox mechanism, which quite probably involves the formation of a radical-ion pair 23 (see Scheme 3).

In studies to learn whether the new heteroorganic ligands obtained could coordinate with a metal atom, we found that imine 11 and azines 14 and 18 readily interact with $(CH_2=CH_2)_2Rh(acac)$.[20] However, the structure of the resultant intensively colored paramag-

netic organometallic products (a signal with $g = 2.0028$ is present in the ESR spectrum) calls for further investigation.

Reactions of functionally substituted amines with conjugated compounds containing a redox-active metal atom in their structure are rather promising for the synthesis of "cascade" type metallocomplexes.[2] In the present work, the possibility of using reactions of this type was first shown by the reaction of complex 24 with hydrazone 13 (Scheme 4). The metallocomplex 25 obtained in this case contains a carbonyl group together with an amino group, which makes it a promising synthon for obtaining other more sophisticated polyconjugated metallocomplexes.

Scheme 4

The structures of all new products obtained were confirmed by the data of elemental analysis, mass spectra, and NMR spectra. The ^{1}H NMR spectra of the systems in question show the marked spin nonequivalence of all four diastereotopic protons of the cyclohexadiene fragment as a result of the introduction of a trigonal nitrogen atom at the exo-position of dienone 9. In contrast, the symmetrical spin system of the initial dienone 9 gives an AA'BB' type ^{1}H NMR spectrum. This can be explained by the hindered internal rotation of the fragments of these molecules with respect to each other about the exo-imine C=N bond after the introduction of the trigonal nitrogen.

Thus, these data taken altogether show the considerable promise of designing new "cascade" type ligands by the combination of semiquinoid and functional structural blocks using the =N— and =N—N= bridging groups.

Experimental

The reactions were monitored by TLC (Silufol UV-254 plates), and the substances were detected in the UV light. NMR spectra were recorded on a Bruker WR-200 SY spectrometer (200.12 MHz for ^{1}H and 50.1 MHz ^{13}C) with the residual protons of deuterated solvents as the internal standard. Mass spectra (EI) were recorded on an MS-890 instrument (energy of ionizing electrons 70 eV). ESR spectra were recorded on a Varian E-12 instrument.

Ketone 9, hydrazone 13, complex 24, 2-amino-5-methylphenol 10, acetylferrocene 16, and 5-methylsalicylaldehyde 17 were obtained following procedures described previously (see Refs. 13,15—18, respectively). The solvents were dried using standard procedures.

5-Methyl-2-(4-methyl-4-trichloromethylcyclohexa-2,5-dienylideneamino)phenol (11). A solution of ketone 9 (4.51 g, 20 mmol) and 2-amino-5-methylphenol 10 (2.46 g, 20 mmol) in toluene (40 mL) was heated to boiling with stirring in the presence of anhydrous Na_2SO_4 (10.0 g) under an argon atmosphere and then refluxed for 2.5 h. The reaction mixture was filtered, the precipitate was washed with hot toluene (2×5 mL), and the combined toluene solutions were concentrated to dryness. The residue (a red-brown oil) was extracted with boiling hexane (100 and 50 mL). The combined hexane extracts were concentrated to 100 mL, cooled to −25 °C, and the yellow-brown needle-shaped crystals formed were filtered off. Recrystallization from hexane with activated carbon gave imine 11 (2.30 g, 34.8%), m.p. 119—120 °C. Found (%): C, 54.21; H, 4.19; N, 4.23. $C_{15}H_{14}Cl_3NO$. Calculated (%): C, 54.49; H, 4.27; N, 4.24. ^{1}H NMR (CDCl$_3$), δ: 1.64 (s, 3 H, CH$_3$ aliph.); 2.32 (s, 3 H, CH$_3$ arom.); 6.60 (br.s, 1 H, OH); 6.64 (dd, 1 H, CH arom., $^3J = 7.9$ Hz, $^4J = 1.2$ Hz); 6.67 (dd, 1 H, CH olef., $^3J = 11.0$ Hz, $^4J = 0.8$ Hz); 6.67 (m, 2 H, CH olef.); 6.74 (d, CH arom., $^3J = 7.9$ Hz); 6.82 (d, 1 H, CH arom., $^4J = 0.8$ Hz); 6.93 (dd, 1 H, CH olef., $^3J = 11.0$ Hz, $^4J = 0.8$ Hz). ^{13}C {^{1}H} NMR (CDCl$_3$), δ: 21.32 (CH$_3$ aliph.); 23.94 (CH$_3$ arom.); 56.30 (C(CH$_3$)CCl$_3$); 105.05 (CCl$_3$); 115.84, 120.1, 120.58, 122.73, 132.35, 132.53, 137.84, 138.78, 141.21, 150.48, 156.20.

The combined hexane mother liquors were concentrated, 5-methyl-2-(para-toluidino)phenol (12) (0.037 g, 0.9%) was isolated by column chromatography of the oil-like residue. ^{1}H NMR (CDCl$_3$), δ: 2.11 (s, 6 H, 2Me); 4.31 (br.s, 1 H, NH); 5.60 (br.s, 1 H, OH); 6.4—7.1 (m, 7 H, CH arom.). MS, m/z (I_{rel} (%)): 213 [M]$^+$ (100), 122 [M—Me—C$_6$H$_4$]$^+$ (8.6).

[1-(4-Methyl-4-trichloromethylcyclohexa-2,5-dienylidene-azino)ethyl]ferrocene (14). Hydrazone 15 (0.240 g, 1 mmol) was added to a solution of acetylferrocene (0.228 g, 1 mmol) in dry EtOH (10 mL). The reaction mixture was stirred for 1 h at 20 °C and then for an additional 2.5 h under reflux. The resulting solution was kept in the refrigerator for 16 h, and then the brick-red-orange precipitate that formed was filtered off, washed with cold EtOH (2×3 mL), and dried to give azine 14 (0.293 g, 65.2%), m.p. 98—99 °C. Found (%): C, 53.87; H, 4.51; Cl, 23.78; Fe, 12.49; N, 6.05; $C_{20}H_{19}Cl_3FeN_2$. Calculated (%): C, 53.43; H, 4.26; Cl, 23.66; Fe, 12.42; N, 6.23. ^{1}H NMR (CDCl$_3$), δ: 1.62 (s, 3 H, CH$_3$ olef., cycle); 2.27 (s, 3 H, MeC=N); 4.20 (c, 5 H, unsubst. Cp); 4.42 (m, 2 H, subst. Cp); 4.75 (m, 1 H, subst. Cp); 4.77 (m, 1 H, subst. Cp); 6.53 (d, 2 H, CH olef., $^3J = 9.6$ Hz); 6.67 (m, 1 H, CH olef.); 7.21 (m, 1 H, CH olef.). ^{13}C {^{1}H} NMR (CDCl$_3$), δ: 15.64 (CH$_3$ olef. cycle); 24.13 (MeC=N); 56.47 (CMeCCl$_3$); 67.66, 67.81, 70.46, 70.48, and 82.65 (subst. Cp); 69.36 (unsubst. Cp), 105.59 (CCl$_3$); 121.34, 129.79, 135.91, 137.79, 150.09 (C=N, cyclohexadiene ring); 163.35 (Cp—C=N).

4-Methyl-4-trichloromethylcyclohexa-2,5-dienone hydrazone (15). A solution of dienone 9 (2.255 g, 10 mmol) and hydrazine hydrate (5.0 g, 100 mmol) in 2-propanol (5 mL) was boiled for 2.5 h. The solvent and excess hydrazine hydrate were removed in vacuo, and the thick yellow-brown oil left was crystallized from hexane at −25 °C following three-fold washing with hot hexane. Hydrazone 15 was obtained (1.368 g, 57.1%). m.p. 85—86 °C. Found (%): C, 39.87; H, 3.28; N, 11.60. $C_8H_9Cl_3N_2$. Calculated (%): C, 40.11; H, 3.79; N, 11.69. ^{1}H NMR (CDCl$_3$), δ): 1.58 (s, 3 H, Me); 5.53 (br.s, 2 H, NH$_2$), 6.16 (dd, 1 H, CH, $^3J = 10.2$ Hz, $^4J = 2.6$ Hz);

6.42 (dd, 1 H, CH, ^3J = 10.2 Hz, ^4J = 1.9 Hz); 6.44 (dd, 1 H, CH, ^3J = 10.5 Hz, ^4J = 2.6 Hz); 6.76 (dd, 1 H, CH, ^3J = 10.5 Hz, ^4J = 1.9 Hz).

4-Methyl-2-(4-methyl-4-trichloromethylcyclohexa-2,5-dienylideneazinomethyl)phenol (18). A solution of hydrazone 15 (0.10 g, 0.42 mmol) in EtOH (4 mL) was added to a solution of 5-methylsalicylaldehyde (17) (0.057 g, 0.42 mmol) in EtOH (5 mL). The mixture was stirred for 1.5 h, the solvent was distilled *in vacuo*, and the yellow oil that formed was crystallized from hexane. Azine 18 (0.134 g, 89.8%) was obtained, m.p. 101.5—102.0 °C. Found (%): C, 54.03; H, 4.25; N, 7.90. $C_{16}H_{15}Cl_3N_2O$. Calculated (%): C, 53.73; H, 4.23; N, 7.83. ^1H (CDCl$_3$), δ: 1.63 (s, 3 H, CH$_3$ aliph.); 2.31 (s, 3 H, CH$_3$ arom.); 6.68 (m, 2 H, CH olef.); 6.70 (m, 1 H, CH olef.); 6.93 (d, 1 H, CH arom., ^4J = 8.3 Hz); 7.13 (d, 1 H, CH arom., ^4J = 1.8 Hz); 7.18 (dd, 1 H, CH arom., ^3J = 8.3 Hz, ^4J = 1.8 Hz); 7.26 (m, 1 H, CH olef.); 8.58 (s, 1 H, CH=N); 11.46 (s, 1 H, OH). ^{13}C {^1H} NMR (CDCl$_3$), δ: 20.27 (CH$_3$ aliph.); 23.92 (CH$_3$ arom.); 56.85 (C(CH$_3$)CCl$_3$), 102.20 (CCl$_3$), 116.70, 117.58, 120.58, 128.73, 129.23, 132.34, 134.11, 138.81, 140.67, 155.41, 157.81, 163.98. MS, m/z (I_{rel} (%)): 356 [M]$^+$ (2.3), 239 [M−CCl$_3$]$^+$ (100).

3,6-Dibromo-9-(para-tolylazo)phenanthren-10-one (21). A solution of hydrazone 15 (0.240 g, 1 mmol) in EtOH (10 mL) was added to a solution of quinone 19 (0.366 g, 1 mmol) in EtOH (60 mL) and DMSO (30 mL) over a period of 5 min at 100—110 °C, and the mixture was stirred for 5 h. The reaction mixture was cooled to −20 °C, the red precipitate that formed was filtered off, washed with hot EtOH (2×5 mL), dried, and monohydrazone 21 (0.086 g, 18.3%) was obtained, m.p. 275 °C (toluene). Found (%): C, 53.62; H, 2.93; Br, 34.17; N, 5.58; $C_{21}H_{14}Br_2N_2O$. Calculated (%): C, 53.65; H, 3.00; Br, 33.99; N, 5.96. ^1H NMR (CDCl$_3$), δ: 2.42 (s, 3 H, Me); 7.26 (d, 2 H, CH tol., ^3J = 9.4 Hz); 7.49 (d, 2 H, CH tol., ^3J = 9.4 Hz); 7.58 (dd, 1 H, phenanthrene, ^3J = 8.7 Hz, ^4J = 1.9 Hz); 7.66 (dd, 1 H, phenanthrene, ^3J = 8.5 Hz, ^4J = 1.7 Hz); 8.21 (d, 1 H, phenanthrene, ^4J = 1.9 Hz); 8.29 (d, 1 H, phenanthrene, ^3J = 8.7 Hz); 8.31 (d, 1 H, phenanthrene, ^3J = 8.5 Hz); 8.31 (d, 1 H, phenanthrene, ^4J = 1.7 Hz); 16.30 (s, 1 H, OH).

The mother liquor was concentrated *in vacuo* to 5 mL at 50—60 °C, and the precipitate that formed was filtered off, washed with Et$_2$O (5 mL), and dried to give a mixture of *cis—trans*-isomers of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone azine (22) (0.066 g, 29.5%) as tiny brilliant gold-colored leaves, m.p. 188—189 °C (EtOH). Found (%): C, 42.73; H, 2.92; N, 6.01. $C_{16}H_{14}Cl_6N_2$. Calculated (%): C, 42.99; H, 3.16; N, 6.27. ^1H NMR (CDCl$_3$), δ: 1.62 (s, 3 H, Me); 6.60 (m, 2 H, CH); 6.69 (m, 1 H, CH); 7.31 (m, 1 H, CH). ^{13}C {^1H} NMR (CDCl$_3$), δ: 24.06 (Me); 56.75 (C(Me)CCl$_3$); 105.27 (CCl$_3$); 121.06 (CH); 129.70 (CH); 137.61 (CH); 137.65 (CH); 139.33 (CH); 153.43 (C=N); 153.55 (C=N).

(4-Methyl-4-trichloromethylcyclohexa-2,5-dienone)(2-hydrazomethyl-4-methylphenolato)rhodium(I) (25). A solution of complex 24 (0.043 g, 0.1 mmol) in C$_6$H$_6$ (2 mL) was added to a solution of hydrazone 13 (0.015 g, 0.1 mmol) in C$_6$H$_6$ (5 mL) over a period of 10 min at −20 °C under argon. The reaction mass turned orange, and a sedimentation of light, yellow precipitate began 10 min after the addition of the whole solution of complex 24. The mixture was stirred for an additional 1 h. The precipitate that formed was filtered off under an argon atmosphere, washed with Et$_2$O (2×2 mL), dried *in vacuo* at 60 °C, and complex 25 (0.030 g, 62.8%) was obtained. Found (%): C, 40.77; H, 3.49; N, 5.58. $C_{16}H_{16}Cl_3N_2O_2Rh$. Calculated (%): C, 40.24; H, 3.38; N, 5.87. ^1H NMR (CDCl$_3$), δ: 2.25 (s, 3 H, CH$_3$ arom.); 2.56 (s, 3 H, CH$_3$ aliph.); 3.88 (m, 1 H, CH olef.); 4.36 (m, 1 H, CH olef.); 4.51 (m, 1 H, CH olef.); 5.00 (m, 1 H, CH olef.); 5.19 (br.s, 2 H,

NH$_2$); 6.91 (d, 1 H, CH arom., ^3J = 8.6 Hz); 6.93 (d, 1 H, CH=N, J_{H-Rh} = 1.8 Hz); 7.21 (dd, 1 H, CH arom., ^3J = 8.6 Hz, ^4J = 2.0 Hz); 7.84 (d, 1 H, CH arom., ^4J = 2.0 Hz). MS, m/z (I_{rel} (%)): 405 [M−2Cl]$^+$ (25.8), 343 [M−CCl$_3$−NH$_2$]$^+$ (37), 149 [M−Rh−(Me(CCl$_3$)C$_6$H$_4$O)]$^+$ (58).

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