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Synthesis and evaluation of a new class of ruthenium-based catalytic systems for atom transfer radical addition and enol ester synthesis

Bob De Clercq, Francis Verpoort *

Department of Inorganic and Physical Chemistry, Division of Organometallic Chemistry and Catalysis, Ghent University, Krijgslaan 281 (S-3), 9000 Ghent, Belgium

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Abstract

We now report the synthesis and characterization of a new class of N-heterocyclic carbene (NHC) and Schiff base containing ruthenium complexes and their performance as catalysts in atom transfer radical addition and enol ester synthesis reactions. The ruthenium Schiff base complexes **3a–f** mediated the atom transfer radical addition (ATRA) of carbon tetrachloride across olefins in excellent yields which markedly depended on the catalyst and the substrate used. Furthermore, dependant on the catalytic system and the reaction conditions used, enol esters or enynes can be obtained in excellent yields with very high selectivities.

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1. Introduction

Ruthenium Schiff base complexes have been well studied by our group over the past 4 years [1]. A wide variety of these organometallic species containing ruthenium–carbon bonds including vinylidene, alkylidene and alkyl substituents have been prepared and these compounds have proven useful for atom transfer radical addition (ATRA) and vinylation reactions [1b,1g,1i,1j,1l,2]. Recently, N-heterocyclic carbene (NHC) groups were successfully introduced as phosphine mimicking ligands in Pd-mediated Heck coupling [3], Suzuki cross-coupling [4], olefin metathesis [5], ATRP [6] and ATRA [6] reactions. NHC's are particularly strong σ-donor but very poor π-acceptor ligands which show little tendency to dissociate from the metal center [7]. Because our previous results pointed out that the electron density on the metal centre is crucial for good catalyst performance of ruthenium Schiff base complexes in enol ester syntheses and vinylation reactions [2], the above-mentioned property of NHC ligands could translate into catalysts of improved reactivity. The ATRA reaction and related processes have become increasingly important in synthetic organic chemistry because the resulting adducts may have an array of multifunctional groups which can be subjected to numerous transformations [3b,8]. Furthermore, the extension of ATRA to ATRP (atom transfer radical polymerization) has recently revitalised the research in this area as well [9]. This reaction consists in the addition of a polyhalogenated alkane across an olefin through a radical mechanism (Scheme 1). This carbon–carbon and carbon–halogen bond-formation is now typically catalyzed by transition metal complexes.

The regioselective addition of carboxylates at the C(1) or C(2) atom of terminal alkynes affords direct access to enol esters of, respectively the anti-Markovnikov and Markovnikov type (Scheme 2) [10]. In spite of their interest as protected aldehyde enolates [11], very few examples of the selective formation of enol esters of the anti-Markovnikov type have been reported.

When taking into account that these unsaturated esters are usually produced in moderate yield from very poisonous vinylmercury derivatives in the presence of palladium acetate as catalyst [12], it is clear that there lies a great challenge in finding more performing alternatives. When performing these enol ester syntheses with ruthenium Schiff base compounds, one has to bear

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* Corresponding author. Tel.: +32-9-2644436; fax: +32-9-2644983. *E-mail address:* francis.verpoort@rug.ac.be (F. Verpoort).

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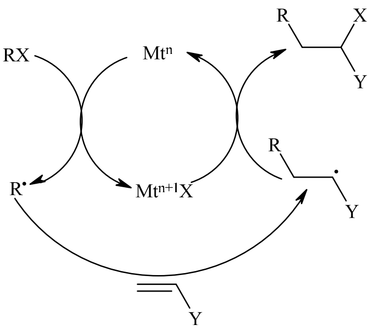


Scheme 1. Schematic representation of the ATRA reaction.

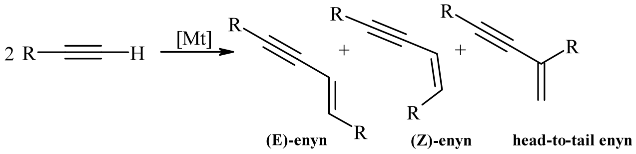
in mind that it is known from literature that a limitation of ruthenium(II) complexes containing a bulky electron-donating bidentate nitrogen ligand is the ability of these complexes to dimerise terminal alkynes into enynes (Scheme 3) [13].

Due to our ongoing research program involving the preparation of new ruthenium Schiff base complexes for applications in ATRA and enol ester syntheses, we have synthesized and characterized a new class of ruthenium Schiff base catalysts containing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand. Moreover, we also assessed the scope of these catalytic systems in ATRA and enol ester syntheses.

2. Results and discussion

2.1. Synthesis of catalysts **3a–f** (Fig. 1)

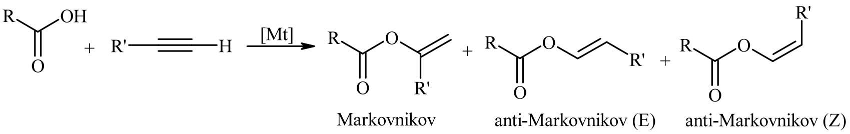
The synthesis and characterization of compounds **1a–f** was reported earlier [1e]. Simple phosphane displacement of the known complexes **1a–f** by bulky 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene afforded compounds **3a–f** in excellent yields as brown solids. Although a number of imidazolylidene compounds are stable as their free carbene, we applied a method that involves the generation of the free imidazolylidene carbene in situ from the tetrafluoroborate salt and KO*t*Bu as base. A suspension of tetrafluoroborate salt **2** in dry THF was prepared in a flame-dried Schlenck flask under nitrogen. One equivalent potassium *tert*-butoxide was added to the rapidly stirred suspension at room temperature, resulting in the immediate dissolution of **2** to form a yellow solution. After 5 min, one equivalent of a solution of **1a–f** in dry toluene was added via a syringe. The mixture was heated to 70–80 °C for 1 h and subsequently cooled to room temperature. After evaporation of the solvent under vacuo, pentane was added and the mixture was cooled to −78 °C. The precipitate was filtered off, washed with cold pentane and dried in vacuo to afford complexes **3a–f** as brown microcrystalline solids in good yields. For the characterization of compounds **3a–f** see Section 4.



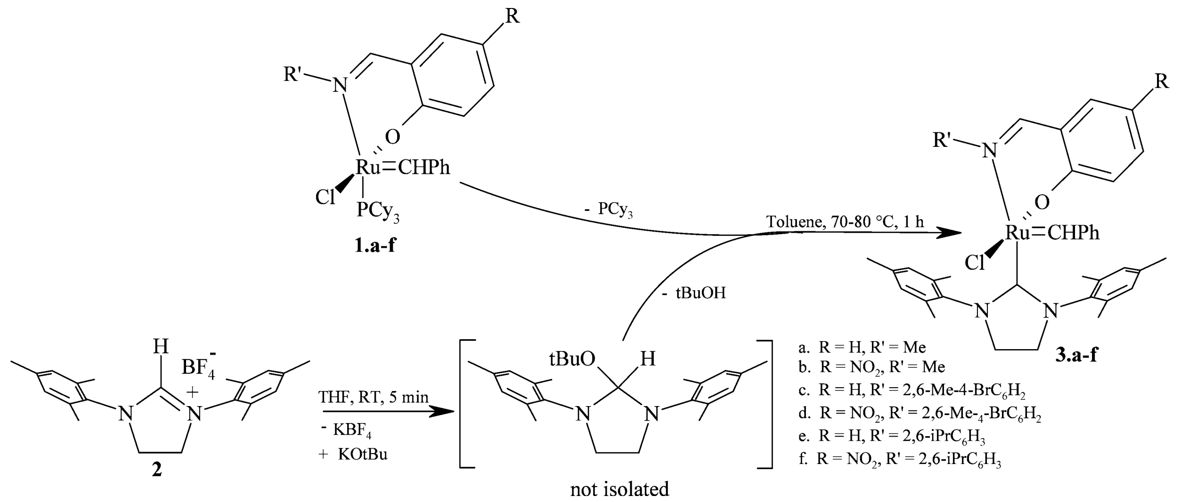
Scheme 3. Schematic representation of metal-catalyzed dimerization reaction of terminal alkynes.

2.2. Atom transfer radical addition reactions (ATRA)

In a first set of experiments, we checked the ability of ruthenium complexes **3a–f** to catalyze ATRA of CCl_4 to seven representative olefins under standardised reaction conditions (Table 1). The results gathered in Table 1 reveal that the outcome of the reaction depended very much on the olefin and catalytic system used. It is clear that the Schiff base ligand should introduce enough steric bulkiness in the catalytic structure in order to have some reasonable catalytic activity. Indeed, the catalytic performance of systems **3a–b** (entries 1 and 2) is much lower compared to compounds **3c–f** (entries 3–6) that contain a more bulky Schiff base, and this irrespective of the olefin used. However, the steric influence of the Schiff base is rather subtle as is demonstrated by the fact that too bulky ligands lead to a decrease in catalytic activity. Indeed, the methyl substituted aromatic Schiff base **3c** (entry 3) reaches systematically higher yields than the isopropyl containing Schiff base **3e** (entry 5). Examination of data from Table 1 further shows that also the electronic properties of these ligands exert a big influence on the catalytic activity of these catalysts. This is best illustrated by comparing the yields of **3a** (entry 1) with **3b** (entry 2), **3c** (entry 3) with **3d** (entry 4) and **3e** (entry 5) with **3f** (entry 6). In each series, the compound containing the electron withdrawing nitro group has the highest catalytic activity. The catalytic system **3d** (entry 4) clearly has the best combination of steric crowding and electronic balance, as this complex exhibits the best catalytic performance of our systems and this for all olefins. For example, when the reaction mixture is



Scheme 2. Schematic representation of enol ester synthesis mediated by transition metal complexes.



a. R = H, R' = Me
b. R = NO_2, R' = Me
c. R = H, R' = 2,6-Me-4-BrC_6H_2
d. R = NO_2, R' = 2,6-Me-$_4$-BrC_6H_2
e. R = H, R' = 2,6-$iPrC_6H_3$
f. R = NO_2, R' = 2,6-$iPrC_6H_3$

Fig. 1. Synthesis of complexes **3a**–**f**.

heated for 8 h at 65 °C, **3d** (entry 4) converts methyl methacrylate (MMA), methyl acrylate (MA) and styrene (Styr.) into the monoadduct in, respectively 85, 70 and 73% yield. Also isobutyl methacrylate (IBMA), butyl acrylate (BA) and diethylallylmalonate (DEAM) are converted smoothly under these reaction conditions, reaching, respectively 78, 67 and 91% yield. When the reaction is performed for 8 h at 85 °C (entry 7) instead of 8 h at 65 °C (entry 4), MMA, IBMA, MA and Styr. are converted in nearly quantitative yields with this catalyst. When working under these reaction conditions, also BA and acrylonitrile (AN) are converted smoothly as the ATRA products are obtained in, respectively 75 and 63% yield. Moreover, even at catalyst loadings of 0.066 mol% the yields remain satisfying (entry 8).

We also succeeded in our intention to optimize catalytic performance of systems **1a**–**f** by replacing the phosphine ligand by a NHC group. Indeed, when comparing the catalytic performance of **1d** (best catalyst in this class) and **3d** (best catalyst in this class), it is clear from the results in Table 1 that system **3d** is much more performing (compare the results of entries 9 and 10 with, respectively entries 4 and 7). The reason for the better activity of complex **3d** (which contains a bulky N-substituent and an electron withdrawing R group) must probably be sought in a more facile one-arm decoordination of the Schiff base ligand [1e] allowing an easy coordination of the substrate on the metal center.

2.3. Vinylation

In a second set of experiments, we conducted vinylation reactions using catalytic systems **3a**–**f**. The results of these tests are depicted in Table 2. When octadiyn is used as a substrate, the addition of carboxylic acids result in the selective formation of (*E*)-alk-1-en-yl esters

Table 1
ATRA of carbon tetrachloride to representative olefins catalyzed by ruthenium complexes **3a**–**f** [a]

Entry	1	2	3	4	5	6	7	8	9	10
Catalyst	**3a** [b]	**3b** [b]	**3c** [b]	**3d** [b]	**3e** [b]	**3f** [b]	**3d** [c]	**3d** [d]	**1d** [e]	**1d** [f]
Methyl methacrylate	22	36	74	85	54	61	96	66	25	51
Isobutyl methacrylate	19	27	69	78	49	53	93	62	18	30
Methyl acrylate	16	33	64	70	41	44	89	60	20	44
n-Butyl acrylate	11	29	60	67	37	43	75	42	16	26
Styrene	20	34	69	73	43	48	84	55	87	98
Acrylonitrile	<5	8	38	46	17	21	63	24	13	21
Diethylallylmalonate	35	43	83	91	61	72	98	70	86	94

[a] Yields (%) based on GLC using dodecane as internal standard.

[b] Reaction conditions. Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures, distilled and kept under nitrogen at −20 °C. The catalyst (0.03 mmol) was dissolved in toluene (1 ml) and subsequently added through a septum to the solution of alkene (9 mmol), CCl_4 (13 mmol), dodecane (0.25 ml) in toluene (3 ml). The reaction mixture was heated at 65 °C for 8 h.

[c] Idem as [b] but here the reaction mixture was heated at 85 °C for 8 h.

[d] Idem as [b] but here the amount of catalyst added was 0.006 mmol.

[e] Idem as [b] but the reaction mixture was heated at 65 °C for 17 h.

[f] Idem as [b] but the reaction mixture was heated at 85 °C for 17 h.

Table 2
Synthesis of enol esters from phenylacetylene, octadiyn and ruthenium catalysts **3a**–**f** [a]

	Total yield (%) [b]	% M. [c]	% Anti-M. (Z) [c]	% anti-M. (E) [c]	% Head-to-tail enyn [c]	% (Z)-enyn [c]	% (E)-enyn [c]		
3a	ph.ac.	f. ac.	69	6	3	12	2	4	73
		ac. ac.	74	10	–	5	3	6	76
3b	ph.ac.	f. ac.	61	7	–	11	5	4	73
		ac. ac.	68	4	2	8	3	3	80
3c	ph.ac.	f. ac.	79	9	3	7	–	5	76
		Ac. ac.	83	7	–	9	–	6	78
3d	ph.ac.	f. ac.	71	9	–	7	–	11	73
		ac. ac.	78	8	–	10	–	3	79
3e	ph.ac.	f. ac.	93	5	–	11	–	3	81
		ac. ac.	99	3	–	14	–	5	78
3f	ph.ac.	f. ac.	86	8	2	9	–	2	79
		ac. ac.	92	7	4	10	–	5	74
							% disubstituted enol ester		
3a	octad.	f. ac.	49	9	7	81		3	
		ac. ac.	56	10	6	78		6	
3b	octad.	f. ac.	37	8	8	80		4	
		ac. ac.	43	11	4	83		2	
3c	octad.	f. ac.	67	9	4	74		3	
		ac. ac.	70	13	5	76		6	
3d	octad.	f. ac.	61	11	3	79		7	
		ac. ac.	66	12	6	78		4	
3e	octad.	f. ac.	73	8	7	79		6	
		ac. ac.	77	9	5	83		3	
3f	octad.	f. ac.	64	11	7	77		5	
		ac. ac.	72	10	8	82		–	

[a] The reactions were carried out by using 4.4 mmol of carboxylic acid, 4.4 mmol of alkyne and 0.04 mmol of catalyst in 3 ml toluene at 100 °C for 4 h under an inert atmosphere.

[b] The total yield was determined with Raman spectroscopy by following the diminishing intensity of the $\nu_{C\equiv C}$ of phenylacetylene (ph. ac.) and octadiyn (octad.) and using a calibration curve. (f. ac. = formic acid, ac. ac. = acetic acid).

[c] The selectivities were determined by ^{1}H-NMR and GC–MS (making use of the different fragmentations of the isomers). GC–MS measurements excluded the formation of other products than those reported here. (% M = percentage Markovnikov addition product, % anti-M = percentage anti-Markovnikov product.)

corresponding to a regio- and stereoselective anti-Markovnikov addition of the acid to the triple bond. The percentage of (E)-alk-1-en-yl ester is for all six catalytic systems and both acids similar and varies in the range of 74–83%. The total yield, however, is very dependant of the type of catalyst and acid used. Now system **3e** is the most active. Whereas with formic acid and acetic acid a total yield of, respectively 37% and 43% is obtained with the worst performing system **3b**, up to 73 and 77% of total conversion is reached with **3e**. Besides the formation of the (E)-alk-1-en-yl ester, also a small percentage of (Z)-alk-1-en-yl ester, Markovnikov addition products and disubstituted enol esters are obtained.

When phenylacetylene is used as alkyne source, the dimerization reaction depicted in Scheme 3 becomes very important. Indeed, with all catalytic systems the alkyne dimerization reaction producing the (E)-enyn is predominant. For example, when using acetic acid the most performing system **3e** produces (besides a modest yield of the Markovnikov addition compound) the (E)-enyn and the (E)-anti Markovnikov addition product with a selectivity of, respectively 78 and 14% yield reaching a total yield of 99%. Concerning the selectivities of the formed reaction products, the same tendency is observed for all the other catalytic systems. Furthermore, with phenylacetylene as the alkyne reaction partner, all the catalytic complexes were devoid of any significant activity for the formation of the head-to-tail enyn. Moreover, also the (Z)-enyn and the (Z) anti-Markovnikov products were observed only as traces. Because the selective dimerization of alkynes is also a useful catalytic reaction [13], a solution of **3e** (0.04 mmol) in toluene (3 ml) was treated with 4.4 mmol phenylacetylene at 100 °C for 4 h and the reaction mixture was monitored by ^{1}H-NMR and GC–MS. Surprisingly, the total yield of the dimerization reaction decreased dramatically when no acid was added (total yield = 31% and exclusive formation of the (E)-enyn). However, the total yield could be improved dramatically by addition of a catalytic amount of acid (0.04 mmol). When using formic and acetic acid, the (E)-enyn was obtained in, respectively 90 and 96% total yield with selectivities of, respectively 84 and 79%.

It deserves to be emphasized that systems **3a**–**f** completely reverse the generally observed regio-selectivity of the addition to terminal alkynes and allow the unprecedented catalytic stereoselective synthesis of *E*-enol esters by direct *cis*-addition of carboxylic acids to terminal alkynes and thus offers the selective transformation of the $-C\equiv CH$ moiety into a potential $-CH_2CHO$ group.

3. Conclusion

In conclusion, we succeeded in synthesizing and characterizing the first ruthenium-based examples of a new class of compounds containing Schiff base groups as well as N-heterocyclic carbenes as ligands and their application as catalysts in ATRA and vinylation reactions. The results obtained point out that catalytic systems **3a**–**f** are highly efficient catalysts for promoting ATRA of CCl_4 to terminal alkenes. Furthermore, dependent on the reaction conditions, they can catalyse the formation of enol esters or enynes in excellent yields with very high stereoselectivities.

4. Experimental

4.1. General considerations

All reactions and manipulations were performed under an argon atmosphere by using conventional Schlenck-tube techniques. Argon gas was dried by passage through P_2O_5 (Aldrich 97%). ^{1}H-NMR spectra (500 MHz) were recorded on a Bruker AM spectrometer. The chemical shifts are reported in ppm and Me_4Si is used as reference compound. The Raman spectrometer was a Bruker Equinox 55 equipment with a FRA 106 module. For ATRA reactions, all reagents and solvents were dried, distilled and stored under nitrogen at −20 °C with conventional methods. GC-analysis is performed using the following conditions: column: SPB™-5; 30 m × 0.25 mm × 0.25 μm film thickness; carrier gas: He, 100 kPa; detector: FID; gas chromatograph: Varian 3300; integrator: Vista 401. GC/MS measurements were performed using the following conditions: column: SPB™-5; 30 m × 0.25 mm × 0.25 μm film thickness; carrier gas: He, 100 kPa; detector: FID; gas chromatograph: Varian 4600; MS: Finnigan MAT ITD. Commercial grade solvents were dried and deoxygenated for at least 24 h over appropriate drying agents under nitrogen atmosphere distilled prior to use. Unless otherwise noted, all other compounds were purchased from Aldrich Chemical Co., and used as received.

4.2. General procedure for ATRA reactions and enol ester syntheses

For entries 1–7, 9 and 10 from Table 1, all reactions were performed by adding 0.01 mmol of the catalyst solution in toluene into a dry 10 ml vessel. Then the solution of alkene (3 mmol), CCl_4 (4.33 mmol) and dodecane (0.083 ml) in toluene (1 ml) were added after which the reaction mixture was heated for 8 or 17 h at the appropriate reaction temperature. For entry 8 from Table 1, the reaction conditions were the same as mentioned before with this difference that here 0.006 mmol of the catalyst solution in toluene was added into the dry 10 ml vessel. The yields were obtained by GC-analysis of the reaction mixture using dodecane as internal standard.

In a typical vinylation experiment, 4.4 mmol of carboxylic acid, 4.4 mmol of alkyn and 0.04 mmol of catalyst solution in toluene were transferred in a 15 ml glass vessel containing 3 ml toluene. Then the reaction mixture was heated for 4 h at 100 °C under an inert atmosphere. The total yield was determined with Raman spectroscopy by following the diminishing intensity of the $\nu_{C\equiv C}$ of phenyl acetylene and octadiyn and using a calibration curve (Conformation was obtained by GC/MS). The selectivity's were determined by GC–MS making use of the different fragmentations of the isomers. GC/MS measurements excluded also the formation of other products than those reported here.

4.3. Characterization

4.3.1. Ruthenium Schiff base complex **3a** (yield: 85%)

^{1}H-NMR ($CDCl_3$): δ 19.91 (s, 1H), 8.94 (d, 1H), 7.55 (t, 1H), 7.48 (d, 2H), 7.25–6.89 (br m, 9H), 6.84 (t, 1H), 3.22 (m, 4H), 3.04 (d, 3H), 2.22 (s, 6H), 2.13 (s, 3H), 1.79 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 295.4 (CHPh), 210.2 (NCN), 163.7 (C=N); Anal. Calc. for $C_{36}H_{40}ClON_3Ru$ (667.39): C, 64.78; H, 6.04; N, 6.32. Found: C, 64.63; H, 6.14; N, 6.34%.

4.3.2. Ruthenium Schiff base complex **3b** (yield: 78%)

^{1}H-NMR ($CDCl_3$): δ 19.96 (s, 1H), 9.02 (d, 1H), 8.29 (d, 1H), 8.17 (d, 1H), 7.55 (d, 2H), 3.25 (m, 4H), 3.09 (d, 3H), 2.63 (s, 6H), 2.24 (s, 6H), 2.14 (s, 3H), 1.83 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 298.7 (CHPh), 214.2 (NCN), 166.4 (C=N); Anal. Calc. for $C_{36}H_{39}ClO_3N_4Ru$ (712.44): C, 60.69; H, 5.52; N, 6.76. Found: C, 60.63; H, 5.61; N, 6.62%.

4.3.3. Ruthenium Schiff base complex **3c** (yield: 71%)

^{1}H-NMR ($CDCl_3$): δ 19.42 (s, 1H), 8.16 (d, 1H), 7.95 (d, 1H), 7.84 (d, 2H), 7.38–7.01 (br m, 9H), 6.97 (s, 1H), 6.94 (s, 1H), 6.91 (d, 1H), 3.18 (m, 4H), 2.49 (s, 6H), 2.31 (s, 3H), 2.20 (s, 6H), 2.09 (s, 3H), 1.76 (s, 3H), 1.72 (d, 3H); ^{13}C-NMR ($CDCl_3$): δ 288.4 (CHPh), 205.6 (NCN), 160.2 (C=N); Anal. Calc. for $C_{43}H_{45}BrClON_3Ru$ (836.4): C, 61.74; H, 5.42; N, 5.05. Found: C, 60.99; H, 5.53; N, 4.92%.

4.3.4. Ruthenium Schiff base complex **3d** (yield: 73%)

^{1}H-NMR ($CDCl_3$): δ 19.51 (s, 1H), 8.19 (d, 1H), 8.05 (d, 1H), 7.88 (d, 2H), 7.44–7.08 (br m, 8H), 7.02 (s, 1H), 6.99 (s, 1H), 6.94 (d, 1H), 3.22 (m, 4H), 2.54 (s, 6H), 2.34 (s, 3H), 2.22 (s, 6H), 2.13 (s, 3H), 1.80 (s, 3H), 1.77 (d, 3H); ^{13}C-NMR ($CDCl_3$): δ 292.3 (CHPh), 209.1 (NCN), 164.6 (C=N); Anal. Calc. for $C_{43}H_{44}BrClO_3N_4Ru$ (881.44): C, 58.59; H, 5.03; N, 6.39. Found: C, 58.76; H 5.17; N, 6.16%.

4.3.5. Ruthenium Schiff base complex **3e** (yield: 70%)

^{1}H-NMR ($CDCl_3$): δ 19.61 (s, 1H), 8.01 (d, 1H), 7.80 (d, 2H), 7.49 (t, 1H), 7.30–6.98 (m, 12H), 6.59 (t, 1H), 3.31 (septet, 1H), 3.11 (m, 4H), 2.54 (s, 6H), 2.27 (s, 6H), 2.15 (s, 3H), 2.06 (septet, 1H), 1.78 (s, 3H), 1.31 (d, 3H), 1.08 (d, 3H), 0.70 (dd, 6H); ^{13}C-NMR ($CDCl_3$) δ 289.7 (CHPh), 209.4 (NCN), 163.6 (C=N); Anal. Calc. for $C_{47}H_{54}ClON_3Ru$ (813.61): C, 69.38; H, 6.69; N, 5.19. Found: C, 68.65; H, 6.82; N, 5.15%.

4.3.6. Ruthenium Schiff base complex **3f** (yield: 73%)

^{1}H-NMR ($CDCl_3$): δ 19.66 (s, 1H), 8.09 (d, 1H), 7.84 (d, 2H), 7.54 (t, 1H), 7.29–6.91 (m, 12H), 6.65 (t, 1H), 3.34 (septet, 1H), 3.15 (m, 4H), 2.86 (s, 1H), 2.33 (s, 6H), 2.22 (s, 3H), 2.11 (septet, 1H), 1.80 (s, 3H), 1.38 (d, 3H), 1.12 (d, 3H), 0.71 (dd, 6H); ^{13}C-NMR ($CDCl_3$): δ 290.9 (CHPh), 214.3 (NCN), 164.1 (C=N); Anal. Calc. for $C_{47}H_{53}ClO_3N_4Ru$ (858.66): C, 65.74; H, 6.22; N, 5.61. Found: C, 65.01; H, 6.32; N, 5.57%.

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