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Highly selective isomerization of *N*-allylamines catalyzed by ruthenium and rhodium complexes

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Abstract

The isomerization of *N*-allylamines ($R^1R^2NCH_2CH{=}CH_2$ and $PhMeNCH_2CH{=}CHSiMe_3$) catalyzed by $[RhH(CO)(PPh_3)_3]$ or $[RuClH(CO)(PPh_3)_3]$ to corresponding 1-propenyl derivatives is described. In the case of the ruthenium complex, double bond migration was successful only in the case of allylamines with bulky groups (Me_3C, Me_3Si, Me_2CH) at the nitrogen atom. A strong *E*-selectivity in the isomerization of allylamines was observed. It is postulated that the *E*-selectivity of double bond migration is the result of a specific coordination of the metal atom by the phenyl substituent or the nitrogen atom. This hypothesis has been confirmed by theoretical calculations (ab initio) performed for some *N*-allylamines and enamines.

Keywords: Double bond migration; *N*-allylamines; Enamines; Selective isomerization; Ruthenium complexes; Rhodium complexes

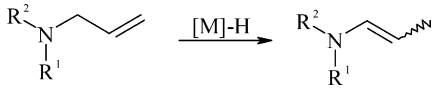
1. Introduction

Double bond migration of *N*-allyl derivatives (*N*-allyl: amines, amides, imides, imines, carbamates, oximes) has been studied extensively. Its meaning for organic synthesis arises from the importance of its products: *N*-(1-propenyl) systems (in general: *N*-vinyl), e.g. enamines, enamides, azadienes. Especially enamines occupy a prominent place as intermediates in organic synthesis [1–5]. For example, stereospecific isomerization of prochiral allylamines using cationic rhodium complexes with chiral ligands (BINAP and derivatives) yields the corresponding chiral enamines [6–11], which can be subsequently hydrolyzed to obtain chiral aldehydes [12]. Ruthenium [13–15], titanium [15,16], iron [17], cobalt [18] molybdenum [19] and, particularly, rhodium complexes [8–10,15,20,21] were applied for the isomerization of *N*-allyl compounds. Moreover, isomerization of *N*-allyl to *N*-(1-propenyl) amines is the key step in the protection and following deprotection of amino groups [22–24].

The present paper deals with the isomerization of various *N*-allylamines catalyzed by ruthenium and rhodium complexes. The reasons of the observed *E*-selectivity in some isomerization reactions have been analyzed and ab initio theoretical calculations were used to explain some of them. Preliminary results of these investigations were described in our previous communication [25].

2. Results and discussion

The isomerization of some *N*-allylamines to corresponding enamines catalyzed by $[RhH(CO)(PPh_3)_3]$ and $[RuClH(CO)(PPh_3)_3]$ was investigated.



The results are summarized in Table 1. For each *N*-allylamine we have been able to choose such a catalyst

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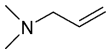
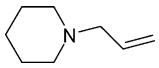
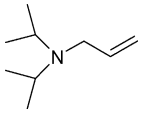
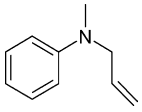
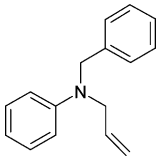
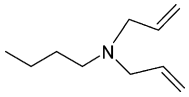
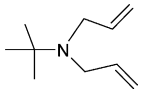
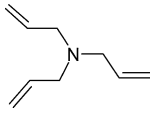
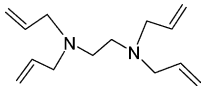
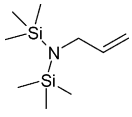
Table 1
Isomerization of *N*-allylamines to enamines catalyzed by [RuClH(CO)(PPh_3)$_3$] ([Ru]) and [RhH(CO)(PPh_3)$_3$] ([Rh])

Entry	*N*-allylamine	*t* [°C]	*τ* [h]	*S*/*C*	So (V)	Enamine	
						y [%][a]	*E*/*Z*[b]
1		60	2	108 [Rh]	C_6H_6 1.1	>98	100/0
2		80	2	73 [Rh]	C_6H_6 0.63	>98	100/0
3		80	2	65 [Rh]	C_6H_6 0.71	>99	100/0
		60	2	67 [Ru][c]	C_6H_6 0.71	>99	100/0
4		60	2	42 [Rh]	C^6H_6 0.74	>99	96/4
5		80	2	41 [Rh]	C_6H_6 1.1	>99	99/1
6		60	2	60 [Rh]	C_6H_6 0.74	>98	92/8/0[c]
		60	2	60 [Ru]	C_6H_6 0.74	26	92/8/0[c]
7		100	3	60 [Rh]	C_6H_6 0.77	>98	95/5/0[c]
		80	2.5	62 [Ru]	C_6H_6 0.77	>98	95/5/1[c]
8		80	2	67 [Rh]	C_6H_6 0.41	>98	87/12/1/0[d]
9		60	2	41 [Rh]	C_6H_6 1.1	>98	83/10/7/0/0[e]
10		120	3	57 [Rh]	C_6H_6 1.1	88	89/11
		100	3	120 [Ru]	C_6H_6 1.1	>98	89/11

S/*C*—substrate:catalyst; So (V)—solvent, ([cm^3 per 1 mmol of substrate]); *y*—yield of the double bond migration product, determined by ^{1}H NMR.
[a] Conversion was always quantitative (determined by ^{1}H NMR and GC–MS).
[b] Determined by ^{1}H NMR and GC–MS.
[c] EE/EZ/ZZ.
[d] EEE/EEZ/EZZ/ZZZ.
[e] EEEE/EEEZ/EEZZ/EZZZ/ZZZZ.

and such reaction conditions that the conversion and selectivity were practically quantitative. Although all reactions described in Table 1 were carried out in benzene, identical results were obtained in THF. [RhH(CO)(PPh_3)$_3$] catalyzed the isomerization of all allylamines under study, whereas [RuClH(CO)(PPh_3)$_3$] only those with bulky groups at the nitrogen atom (*i*-Pr, *t*-Bu or Me_3Si). If the nitrogen atom is not shielded by bulky substituents, no double bond migration takes place in the presence of [RuClH(CO)(PPh_3)$_3$]. Raising the temperature of the reaction leads to the formation of many products-less than 20% of these are actually enamines. It is interesting that a high *E*-selectivity of allylamine isomerization has been observed both in the presence of a rhodium and a ruthenium complex. This

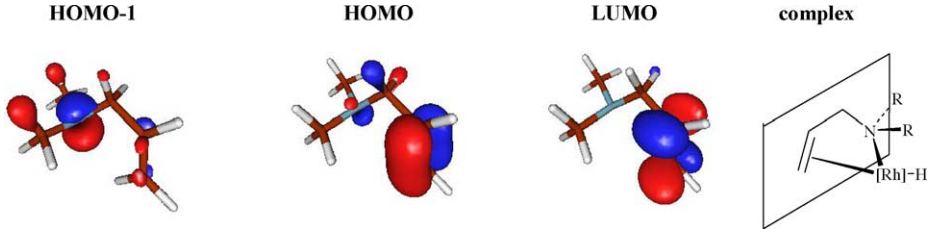


Fig. 1. Selected molecular orbitals of *N*-allyl-*N*,*N*-dimethylamine. Postulated coordination mode of the rhodium atom by *N*-allylamines.

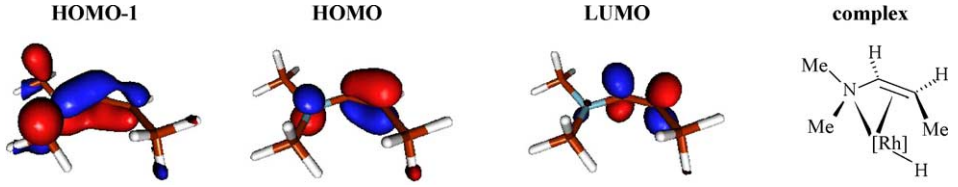


Fig. 2. Selected molecular orbitals of (*Z*)-*N*,*N*-dimethyl(1-propenyl)amine. Postulated structure of the complex formed with the *Z* isomer.

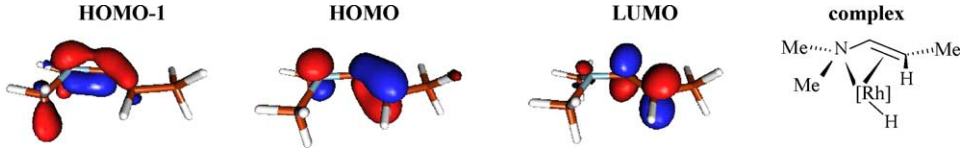


Fig. 3. Selected molecular orbitals of (*E*)-*N*, *N*-dimethyl(1-propenyl)amine. Postulated coordination of the rhodium atom by (*E*)-*N*-(1-propenyl)amines.

fact indicates that the origin of stereoselectivity might be similar. In order to explain the high *E*-selectivity of isomerization of some *N*-allylamines, quantum chemical calculations were performed for *N*,*N*-dimethylallylamine, *N*-allyl-*N*-methylaniline and products of their isomerization, i.e. (*E*)- and (*Z*)-*N*,*N*-dimethyl(l-propenyl)amine and *N*-methyl-*N*-(l-propenyl)aniline (see the experimental section). All the geometries were optimized on the MP2/6-31G(d,p) level. Shapes of these molecular orbitals (i.e. RHF canonical orbitals) of allylamine and both enamines which, in our opinion, may be involved in the coordination of the metal atom are shown in Figs. 1–6. Furthermore, we suggest possible

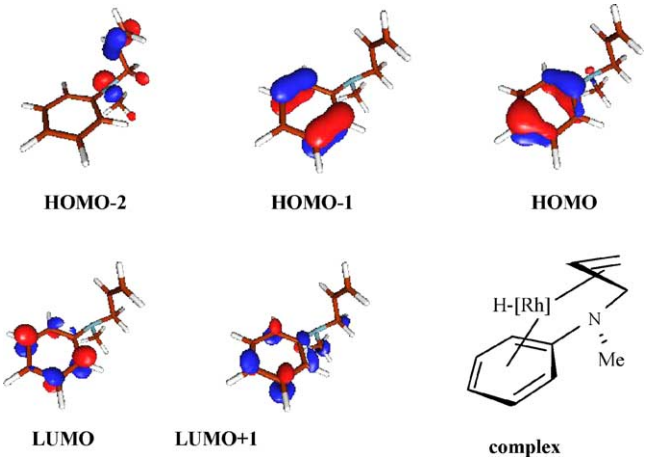


Fig. 4. Selected molecular orbitals of *N*-allyl-*N*-methylaniline. A suggestion of a possible coordination of the substrate.

structures of complexes with a coordinated substrate or product. Such complexes are formed in the catalytic cycle. In our opinion, the contribution of the nitrogen atom to coordinate the metal has a profound impact on the stereochemistry of the product of double bond migration. A similar effect was observed in the isomerization of *N*,*N*-diethylgeranylamine catalyzed by cationic rhodium complexes [6–11]. On the other hand, in the case of aniline derivatives (entry 4 and 5) the stereochemistry of the product is determined by the participation of the phenyl ring in the coordination of the rhodium atom. An analogous effect has been observed by us previously in the case of *E*-stereoselective isomerization of *N*-allyl-*N*-arylethanamides catalyzed by ruthenium and rhodium complexes [26,27]. It is important to note that both the nitrogen atom and the phenyl substituent may be coordinated by the metal atom also in σ-carbyl complexes formed in the course of the reaction. An analysis of ball-and-stick models supports this hypothesis. Thus, the specific coordination may be sustained during the whole reaction pathway.

The decrease in (*E*)-selectivity of isomerization of amine **10** is due to the steric influence of Me_3Si groups, which hinder the participation of the nitrogen atom in the coordination of the metal atom. Probably in the case of that amine, the nitrogen atom does not form a bond with the metal (because of steric interactions). On the other hand, amines **6**–**9** can coordinate through both the nitrogen atom and the double bond of allyl (and 1-propenyl) fragments in so many various ways that it is difficult to predict the stereoselectivity using this simple explanation.

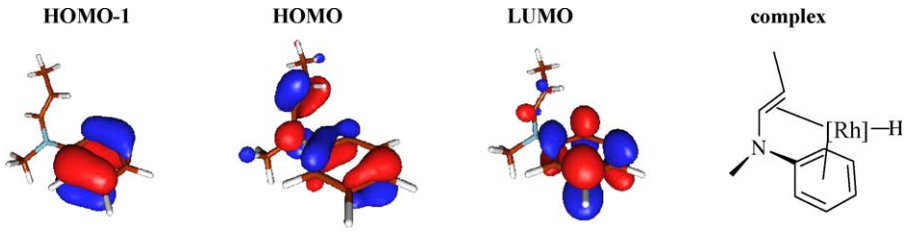


Fig. 5. Selected molecular orbitals of (*E*)-*N*-methyl-*N*-(l-propenyl)aniline. Postulated structure of a complex formed with the catalyst.

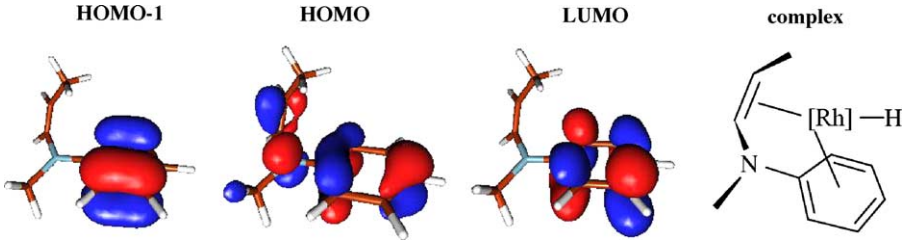
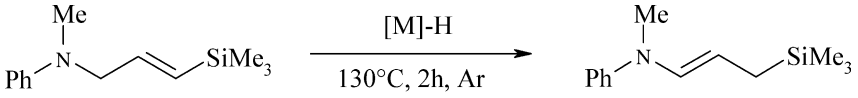
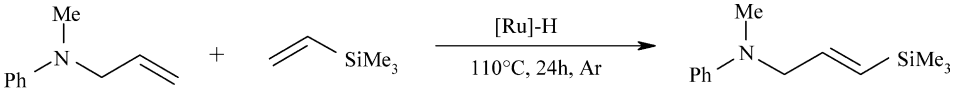


Fig. 6. Selected molecular orbitals of (*Z*)-*N*-methyl-*N*-(1-propenyl)aniline. Postulated structure of a complex with the catalyst.



[M]-H = 5% mol. [RhH(CO)(PPh$_3$ $_3$]; conversion = 100%

Fig. 7. Isomerization of the silylated *N*-allylamine.



[Ru]-H = 0.2% mol [RuClH(CO)(PCy$_2$]; isolated yield = 65%

Fig. 8. Synthesis of the silylated *N*-allylamine.

In our discussion about stereoselectivity we assume that double bond migration in allylamines catalyzed by [RhH(CO)(PPh$_3$)$_3$] and [RuHCl(CO)(PPh$_3$)$_3$] occurs in accordance with the classical hydride mechanism. In our previous work on the isomerization of allylamides and allyl ethers catalyzed by [RuHCl(CO)(PPh$_3$)$_3$] we proved hydride mechanism in double bond migration. Furthermore, it has been proved that the isomerization of alkenes in the presence of [RhH(CO)(PPh$_3$)$_3$] complies with the hydride mechanism, too [28,29]. Moreover, it was demonstrated that the isomerization of an *N*-allylamine containing a trimethylsilyl group at the double bond is possible, see Fig. 7. This finding broadens the scope of applications of these isomerization reactions in organic syntheses. It is worth noting that in the case of (*E*)-*N*-methyl-*N*-phenyl-*N*-(3-trimethylsilyl-2-propenyl)amine a high (*E*)-selectivity of double bond migration was observed. This confirms our earlier statement, that *N*-allyl-*N*-aryl systems isomerize to (*E*)-1-propenyl derivatives [27].

The silylated amine was obtained via silylative coupling of *N*-allyl-*N*-methylaniline with trimethylvinylsilane in the presence of a ruthenium catalyst, see Fig. 8.

It should be emphasized that the silylative coupling was also highly *E*-selective. Probably the stereoselectivity is determined by coordinating effects, as in the previous case. Some stages of the mechanisms of both double bond migration and silylative coupling are identical or similar [30]. Moreover, a high *E*-stereoselectivity of silylative coupling was also observed in other cases [30,31].

3. Conclusion

Several enamines have been obtained via isomerization of allylamines catalyzed by [RuClH(CO)(PPh$_3$)$_3$] and [RhH(CO)(PPh$_3$)$_3$]. The observed high *E*-selectivity

of double bond migration in some *N*-allylamines is the result of specific coordination effects. Theoretical calculations performed for *N*-allyl-*N*,*N*-dimethylamine, (*E*)-*N*,*N*-dimethyl(1-propenyl)amine and (*Z*)-*N*,*N*-dimethyl(1-propenyl)amine are fully consistent with that explanation.

4. Experimental

4.1. Materials

Amines, allyl chloride, allyl bromide were from Aldrich. Solvents were dried with appropriate drying agents (molecular sieves (3 or 4 Å), Na, CaH_2) and distilled prior to use. *N*-allyldimethylamine was purchased from Fluka, *N*-allylcyclohexylamine was from Aldrich, *N*-allylpiperidine from Lancaster, triallylamine from Merck.

(*E*)-*N*-methyl-*N*-phenyl-*N*-(3-trimethylsilyl-2-propenyl) amine: $[RuHCl(CO)(PCy)_2]$ (30 mg; 0.041 mmol), vinyl trimethylsilane (0.41 g; 4.1 mmol), *N*-allyl-*N*-methylaniline (3.01 g; 20.5 mmol) and 1 cm^3 of toluene were heated for 24 h at 110 °C under argon in a 20 cm^3 sealed ampoule. The mixture was chromatographed on a column containing silica sand with hexane-methyl acetate (50:1) as eluent. Crude amine was distilled under reduced pressure to give 0.65 g (65% yield) of the title compound.

N-allyl-*N*,*N*-diisopropylamine, *N*-allyl-*N*-methyl aniline, *N*,*N*-diallyl-*N*-*n*-butylamine and *N*-allyl-*N*,*N*-bis(trimethylsilyl)amine were synthesized as described in literature [32–35].

N-allyl-*N*-benzylaniline: *N*-allylaniline (20 cm^3; 0.150 mol) was refluxed for 2 h with benzyl chloride (18 cm^3; 0.160 mol). Then 20% aq. NaOH was added, until pH was neutral. The product was extracted with 100 cm^3 of toluene. The extract was then washed with water and dried with anhydrous magnesium sulphate. The volatiles were distilled off with a vacuum evaporator and the crude amine was distilled under reduced pressure to give 19 cm^3; (0.085 mol) (57% yield) of the title compound.

N,*N*-diallyl-*N*-*t*-butylamine: *t*-Butylamine (105 cm^3; 1 mol) and then acetic anhydride (94 cm^3; 1 mol) were added to glacial acetic acid (100 cm^3), stirred with a mechanical stirrer for 3 h at r.t., and next refluxed for 1 h. After that the acetic acid was distilled off and the obtained *N*-*t*-butylethanamide was recrystallized from diethyl ether (40% yield). The amide (27 g; 0.23 mol) was refluxed with allyl bromide (120 cm^3; 1 mol), powdered NaOH (50 g; 0.12 mol) and $Bu_4N^+HSO_4^-$ (2 g; 0.006 mol) for 2 h. The mixture was extracted twice with 100 cm^3 hexane and the extract was dried with anhydrous magnesium sulfate. After all volatiles had been distilled off (with a vacuum evaporator), the residue was distilled under reduced pressure.

4.1.1. N-allyl-N,N-diisopropylamine

MS (70 eV) *m*/*e* (int[%]): 140 (14) M^+; 126 (1 0 0); 114 (3); 110 (1); 98 (7); 84 (28); 67 (3); 56 (6). ^{1}H NMR ($CDCl_3$): δ = 5.83 (ddt, 1H, J = 17.1, 10.2, 6.0 Hz, $-CH_2CH{=}CH_2$), 5.15 (ddt, 1H, J = 17.1, 1.2, <0.9 Hz, $-CH_2CH{=}CH_2$-*trans*), 4.99 (ddt, 1H, J = 10.2, 1.2, <0.9 Hz, $-CH_2CH{=}CH_2$-*cis*), 3.10 (ddd, 2H, J = 6.0, <0.9, <0.9 Hz, $-CH_2CH{=}CH_2$), 3.04 (septet, 2H, J = 6.3 Hz, $-CH(CH_3)_3$), 1.01 (d, 12H, J = 6.3 Hz, $-CH(CH_3)$). ^{13}C NMR ($CDCl_3$): δ = 140.1 ($-CH_2-CH{=}CH_2$); 114.6 ($-CH{=}CHCH_3$); 48.2 ($-CH_2-CH{=}CH_2$); 23.4 ($-CH(CH_3)_3$); 20.7 ($-CH(CH_3)_3$).

4.1.2. N,N-diallyl-N-n-butylamine

MS (70 eV) *m*/*e* (int[%]): 153 (19) M^+; 126 (3); 110 (100); 84 (8); 77 (5); 68 (100); 55 (21). ^{1}H NMR (C_6D_6): δ = 5.85 (ddt, 1H, J = 17.1, 10.2, 6.6 Hz, $-CH_2CH{=}CH_2$), 5.15 (ddt, 1H, J = 17.1, 1.2, <0.9 Hz, $-CH_2CH{=}CH_2$-*trans*), 5.10 (ddt, 1H, J = 10.2, 1.2, <0.9 Hz, $-CH_2CH{=}CH_2$-*cis*), 3.07 (ddd, 2H, J = 6.6, <0.9, <0.9 Hz, $-CH_2CH{=}CH_2$), 2.41 (*t*, 2H, J = 7.2 Hz, $-CH_2-CH_2-CH_2-CH_3$), 1.42 (*tt*, 2H, J = 7.2, 6.6 Hz, $-CH_2-CH_2-CH_2-CH_3$), 1.25 (tq, 2H, J = 7.2, 6.6 Hz, $-CH_2-CH_2-CH_2-CH_3$), 0.90 (*t*, 3H, J = 7.2 Hz, $-CH_2-CH_2-CH_2-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 135.8 ($-CH_2-CH{=}CH_2$); 116.9 ($-CH{=}CHCH_3$); 56.8 ($-CH_2-CH{=}CH_2$); 52.4 ($-CH_2-CH_2-CH_2-CH_3$); 29.0 ($-CH_2-CH_2-CH_2-CH_3$); 20.5 ($-CH_2-CH_2-CH_2-CH_3$); 13.9 ($-CH_2-CH_2-CH_2-CH_3$).

4.1.3. N,N-diallyl-N-tert-butylamine

bp = 51–51 °C/2 mmHg. MS (70 eV) *m*/*e* (int[%]): 153 (2) M^+; 126 (3); 110 (100); 84 (8); 68 (5); 55 (2). ^{1}H NMR ($CDCl_3$): δ = 5.87 (ddt, 1H, J = 17.1, 10.2, 6.3 Hz, $-CH_2CH{=}CH_2$), 5.11 (ddt, 1H, J = 17.1, 1.2, <0.9 Hz, $-CH_2CH{=}CH_2$–*trans*), 5.01 (ddt, 1H, J = 10.2, 1.2, <0.9 Hz, $-CH_2CH{=}CH_2$-*cis*), 3.19 (ddd, 2H, J = 6.3, <0.9, <0.9 Hz, $-CH_2CH{=}CH_2$), 1.10 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ = 138.7 ($-CH_2-CH{=}CH_2$); 115.2 ($-CH_2-CH{=}CH_2$); 54.8 ($-C(CH_3)_3$); 51.5 ($-CH_2-CH{=}CH_2$); 27.6 ($-C(CH_3)_3$).

4.1.4. (E)-N-methyl-N-phenyl-N-(3-trimethylsilyl-2-propenyl)amine

bp = 110–115 °C/1 mmHg. MS (70 eV) *m*/*e* (int[%]): 219 (76) M^+; 204 (13); 189 (5); 174 (3); 146 (54); 132 (10); 120 (100); 104 (13); 91 (2); 77 (10); 51 (4). ^{1}H NMR (C_6D_6): δ = 7.18 (ddd, 2H, $J_{2-3} = J_{5-6}$ = 8.4, $J_{3-4} = J_{4-5}$ = 7.5, J_{3-5} = 1.0 Hz, $H_{3\text{-arom}}$ and $H_{5\text{-arom}}$), 6.73 (dd, 1H, $J_{3-4} = J_{4-5}$ = 7.5, $J_{2-4} = J_{4-6}$ = 1.0 Hz, $H_{4\text{-arom}}$), 6.61 (dd, 2H, $J_{2-3} = J_{2-6}$ = 8.4, $J_{2-4} = J_{4-6}$ = 1.0 Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 5.90 (dt, 1H, J = 18.6, 4.2 Hz, $-CH_2CH{=}CH-$), 5.75 (dt, 1H, J = 18.6, 1.5 Hz, $-CH_2CH{=}CH-$), 3.61 (dd, 2H, J = 4.2, 1.5 Hz, $-CH_2CH{=}CH-$), 2.58 (s, 3H, $-CH_3$), 0.19 (s, 9H, $-Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ = 149.6 ($C_{1\text{-arom}}$); 141.6 ($-CH_2CH{=}CH-$); 131.1 ($-CH_2CH{=}CH-$); 129.0 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 116.2 ($C_{4\text{-arom}}$); 112.3 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 57.6 ($-CH_2CH{=}CH-$); 38.0 ($-CH_3$); −1.2 ($-Si(CH_3)_3$).

Table 2
Mean and maximum absolute deviations of bond lengths, valence angles and torsional angles in *N*,*N*-dimethylallylamine (C_1 symmetry) between various levels of theory

	Bond length deviation [Å]		Angle deviation [°]		Torsional angle deviation [°]	
	Mean	Maximum	Mean	Maximum	Mean	Maximum
PM3 and RHF/6–31G(d,p)	0.018	0.044	0.79	2.21	1.91	14.4
RHF/6–31G(d,p) and MP2/6–31G(d,p)	0.007	0.020	0.73	1.87	1.03	4.52
MP2/6–31G(d,p) and MP2/6–311G(2df,2p)	0.002	0.066	0.25	0.46	0.59	2.41
PM3 and MP2/6–31G(d,p)	0.012	0.034	0.89	3.11	2.26	12.2
PM3 and MP2/6–311G(2df,2p)	0.012	0.041	1.00	3.34	2.74	14.6
RHF/6–31G(d,p) and MP2/6–311G(2df,2p)	0.005	0.014	0.71	2.02	1.04	4.99

4.2. Ruthenium and rhodium complexes

$[RuClH(CO)(PPh_3)_3]$ [36], $[RhH(CO)(PPh_3)_3]$ [37] were obtained according to the methods known in literature.

4.3. Enamines (general procedure)

N-allylamines were heated with $[RhH(CO)(PPh_3)_3]$ or $[RuClH(CO)(PPh_3)_3]$ (with or without a solvent) in an argon atmosphere in high-pressure glass ampoules, which were put in a thermostat (±0.1 °C). The proportions of the substrate, catalyst and solvent are given in Table 2. After the reaction had been completed, pentane was added and the mixture was cooled down to −70 °C. Precipitated rhodium compounds, PPh_3 and its oxide were filtered off. Pentane was evaporated from the eluate on a vacuum evaporator. Pure enamines were obtained in 55–95% yields. The separation of (*E*)-*N*,*N*-dimethyl(1-propenyl)amine from the solvent by evaporation was found to be impossible because of its low boiling point.

4.3.1. (E)-N,N-dimethyl-(1-propenyl)amine

MS (70 eV) *m*/*e* (int[%]): 85 (96) M^+; 72 (24); 69 (51); 55 (100). ^{1}H NMR (C_6D_6): δ = 5.83 (dq, 1H, J = 13.2, 1.5 Hz, –C*H*=CHCH$_3$), 4.20 (dq, 1H, J = 13.2, 6.3 Hz, –CH=C*H*CH$_3$), 2.30 (s, 6H, –C*H*$_3$) 1.71 (dd, 3H, J = 6.3, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (C_6D_6): δ = 141.2 (–*C*H=CHCH$_3$); 93.7 (–CH=*C*HCH$_3$); 40.9 (–*C*H$_3$); 15.6 (–CH=CH*C*H$_3$).

4.3.2. (E)-N-(1-propenyl)piperidine

MS (70 eV) *m*/*e* (int[%]): 125 (51) M^+; 110 (100); 96 (17); 84 (4); 82 (19); 68 (25); 55 (8). ^{1}H NMR (C_6D_6): δ = 5.81 (dq, 1H, J = 13.5, 1.2 Hz, –C*H*=CHCH$_3$), 4.23 (dq, 1H, J = 13.5, 6.3 Hz, –CH=C*H*CH$_3$), 2.61 (*t*, 6H, J = 6.00 Hz, –NC*H*$_2$CH$_2$CH$_2$–), 1.70 (dd, 3H, J = 6.3, 1.2 Hz, –CH=CHC*H*$_3$), 1.4 (*tt*, 6H, J = 6.00, 5.1 Hz, –NCH$_2$C*H*$_2$CH$_2$–), 1.29 (*t*, 3H, J = 5.1 Hz, –NC*H*$_2$CH$_2$C*H*$_2$–). ^{13}C NMR (C_6D_6): 5 = 141.7 (–*C*H=CHCH$_3$); 94.5 (–CH=*C*HCH$_3$); 50.2 (–N*C*H$_2$CH$_2$CH$_2$–); 25.8 (–NCH$_2$*C*H$_2$CH$_2$–); 24.8 (–NCH$_2$CH$_2$*C*H$_2$–); 15.8 (–CH=CH*C*H$_3$).

4.3.3. (E)-N,N-diisopropyl-N-(1-propenyl)amine

MS (70 eV) *m*/*e* (int[%]): 140 (7) M^+; 126 (100); 114 (3); 98 (4); 84 (66); 67 (6); 56 (9). ^{1}H NMR ($CDCl_3$): δ = 6.01 (dq, 1H, J = 13.5, 1.2 Hz, –C*H*=CHCH$_3$), 4.23 (dq, 1H, J = 13.5, 6.3 Hz, –CH=C*H*CH$_3$), 3.31 (septet, 2H, J = 6.9 Hz, –CH(C*H*$_3$)$_3$), 1.80 (dd, 3H, J = 6.3, 1.2 Hz, –CH=CHC*H*$_3$), 0.97 (d, 12H, J = 6.9 Hz, –C*H*(CH$_3$)$_3$). ^{13}C NMR (C_6D_6): δ = 132.4 (–*C*H=CHCH$_3$); 89.7 (–CH=*C*HCH$_3$); 45.7 (–*C*H(CH$_3$); 21.5 (–CH(*C*H$_3$)), 16.5 (–CH=CH*C*H$_3$).

4.3.4. (E)-N-methyl-N-(1-propenyl)aniline

MS (70 eV) *m*/*e* (int[%]): 147 (100) M^+; 131 (17); 117 (11); 104 (18); 91 (16); 77 (23); 65 (4); 51 (14). ^{1}H NMR ($CDCl_3$): 5 = 7.24 (ddd, 2H, $J_{2–3}$ = $J_{5–6}$ = 8.5, $J_{3–4}$ = $J_{4–5}$ = 7.3 Hz, $J_{3–5}$ = 1.5 Hz, $H_{3\text{-arom}}$ and $H_{5\text{-arom}}$), 6.91 (dd, 2H, $J_{2–3}$ = $J_{5–6}$ = 8.5 Hz, $J_{2–4}$ = $J_{4–6}$ = 1.0 Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 6.83 (dd, 1H, $J_{3–4}$ = $J_{4–5}$ = 7.3 Hz, $J_{2–4}$ = $J_{4–6}$ = 1.0 Hz, $H_{4\text{-arom}}$), 6.58 (dq, 1H, J = 13.4, 1.5 Hz, –C*H*=CHCH$_3$), 4.65 (dq, 1H, J = 13.4, 6.6 Hz, –CH=C*H*CH$_3$), 3.06 (s, 3H, –C*H*$_3$), 1.74 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ = 148.1 ($C_{1\text{-arom}}$); 134.1 ($C_{4\text{-arom}}$); 129.3 (–*C*H=CHCH$_3$); 119.9 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 116.5 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 98.4 (–CH=*C*HCH$_3$); 34.8 (–*C*H$_3$); 15.7 (–CH=CH*C*H$_3$).

4.3.5. (E)-N-benzyl-N-(1-propenyl)aniline

MS (70 eV) *m*/*e* (int[%]): 223 (100) M^+; 208 (9); 196 (27); 180 (10); 146 (25); 132 (27); 117 (5); 104 (30); 91 (93), 77 (31); 65 (21); 51 (15). ^{1}H NMR ($CDCl_3$): δ = 7.45–6.70 (m, 10H, H_{arom}), 6.64 (dq, 1H, J = 13.8,), 1.5 Hz, –C*H*=CHCH$_3$), 4.58 (dq, 1H, J = 13.8, 6.6 Hz, –CH=C*H*CH$_3$), 4.56 (s, 3H, –C*H*$_2$–), 1.58 (dd, 3H, J = 6.6, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ = 144.5 ($C_{1\text{-arom-phenyl}}$); 138.5 ($C_{1\text{-arom-benzyl}}$); 132.1 (–*C*H=CHCH$_3$); 119.9–126.5 (C_{arom}); 100.0 (–CH=*C*HCH$_3$); 52.0 (–*C*H$_2$–); 15.6 (–CH=CH*C*H$_3$).

4.3.6. (E,E)-N-butyl-N,N-di(1-propenyl)amine

MS (70 eV) *m*/*e* (int[%]): 167 (1) M^+; 153 (100); 138 (36); 124 (51); 110 (35); 96 (29); 82 (56); 77 (4); 68 (40); 57 (19). ^{1}H NMR (C_6D_6): δ = 5.93 (dq, 1H, J = 13.8, 1.5 Hz, –C*H*=CHCH$_3$), 4.36

(dq, 1H, J = 13.8, 6.9 Hz, –CH=C*H*CH_3), 3.05 (*t*, 2H, J = 7.5 Hz, –C*H*$_2$-CH_2–CH_2–CH_3), 1.66 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$), 1.44 (*tt*, 2H, J = 7.2, 6.9 Hz, –CH_2–C*H*$_2$–CH_2–CH_3), 1.17 (tq, 2H, J = 7.2, 6.9 Hz, –CH_2–CH_2–C*H*$_2$–CH_3), 0.82 (*t*, 3H, J = 7.5 Hz, –CH_2–CH_2–CH_2–C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ = 134.9 (–*C*H=$CHCH_3$); 93.8 (–CH=*C*HCH_3); 46.8 (–*C*H_2–CH_2–CH_2–CH_3); 28.2 (–CH_2–*C*H_2–CH_2–CH_3); 20.7 (–CH_2–CH_2–*C*H_2–CH_3); 15.6 (–CH=CH*C*H_3); 14.1 (–CH_2-CH_2-CH_2-*C*H_3).*(E,Z)-N-butyl-N,N-di(1-propenyl)amine*. MS (70 eV) *m*/*e* (int[%]): 167 (1) M^+; 153 (100); 138 (36); 124 (52); 110 (34); 96 (31); 82 (61); 77 (3); 68 (39); 57 (19). ^{1}H NMR (C_6D_6): δ = 6.86 (dq, 1H, J = 13.8, 1.5 Hz, –C*H*=$CHCH_3$), 5.65 (dq, 1H, J = 7.2, 1.5 Hz, –C*H*=$CHCH_3$), 4.51 (dq, 1H, J = 7.2, 6.9 Hz, –CH=C*H*CH_3), 4.36 (dq, 1H, J = 13.8, 6.9 Hz, –CH=C*H*CH_3), 3.05 (*t*, 2H, J = 7.5 Hz, –C*H*$_2$–CH_2–CH_2–CH_3-*trans*), 3.00 (*t*, 2H, J = 7.5 Hz, –C*H*$_2$–CH_2–CH_2–CH_3-*cis*), 1.68 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*cis*), 1.66 (dd, 3H, J = 6.9, 1.5 Hz, –CH=CHC*H*$_3$-*trans*), 1.44 (*tt*, 2H, J = 7.2, 6.9 Hz, –CH_2–C*H*$_2$–CH_2–CH_3), 1.17 (tq, 2H, J = 7.2, 6.9 Hz, –CH_2–CH_2–C*H*$_2$–CH_3), 0.82 (*t*, 3H, J = 7.5 Hz, –CH_2–CH_2–CH_2–C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ = 134.9 (–*C*H=$CHCH_3$-*trans*); 134.6 (–*C*H=$CHCH_3$-*cis*); 104.1 (–CH=*C*HCH_3-*cis*); 93.8 (–CH=*C*HCH_3-*trans*); 51.1 8 (–*C*H_2–CH_2–CH_2–CH_3-*cis*); 46.8 (–CH_2–CH_2–*C*H_2–CH_3-*trans*); 30.7 (–CH_2–*C*H_2–CH_2–CH_3-*cis*); 28.2 (–CH_2–*C*H_2–CH_2–CH_3-*trans*); 20.7 (–CH_2–CH_2–CH_2–*C*H_3-*trans*); 20.4 (–CH_2–CH_2–*C*H_2–CH_3-*cis*); 15.6 (–CH=CH*C*H_3-*trans*); 14.1 (–CH_2–CH_2–CH_2–*C*H_3); 13.1 (–CH=CH*C*H_3-*cis*).

4.3.7. (E,E)-N-t-butyl-N,N-di(1-propenyl)amine

MS (70 eV) *m*/*e* (int[%]): 153 (100) M^+; 138 (45); 108 (2); 98 (20); 8 (46); 68 (38); 57 (15). ^{1}H NMR (C_6D_6): δ = 5.97 (dq, 2H, J = 13.8, 1.2 Hz, –C*H*=$CHCH_3$), 4.96 (dq, 2H, J = 13.8, 6.9 Hz, –CH=C*H*CH_3), 1.66 (dd, 6H, J = 6.9, 1.2 Hz, –CH=CHC*H*$_3$), 1.08 (s, 9H, –C(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ = 132.8 (–*C*H=$CHCH_3$); 109.7 (–CH=*C*HCH_3); 54.6 (–*C*$(CH_3)_3$); 28.7 (–C(*C*H_3)$_3$); 15.1 (–CH=CH*C*H_3).*(E,Z)-N-t-butyl-N,N-di(1-propenyl)amine*. MS (70 eV) *m*/*e* (int[%]): 153 (100) M^+; 138 (34); 108 (5); 98 (26); 8 (40); 68 (16); 57 (5). ^{1}H NMR (C_6D_6): δ = 6.14 (dq, 1H, J = 13.5, 1.2 Hz, –C*H*=$CHCH_3$-*trans*), 5.66 (dq, 1H, J = 7.8, 1.8 Hz, –C*H*=$CHCH_3$-*cis*), 5.23 (dq, 1H, J = 6.9, 6.6 Hz, –CH=C*H*CH_3-*cis*), 4.45 (dq, 1H, J = 13.5, 6.6 Hz, –CH=C*H*CH_3-*trans*), 1.73 (dd, 3H, J = 6.6, 1.2 Hz, –CH=CHC*H*$_3$-*trans*), 1.54 (dd, 3H, J = 6.9, 1.8 Hz, –CH=CHC*H*$_3$-*cis*),1.09 (s, 9H, –C(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ = 132.8 (–*C*H=$CHCH_3$-*trans*); 130.3 (–*C*H=$CHCH_3$-*cis*); 122.1 (–CH=*C*HCH_3-*cis*); 98.5 (–CH=*C*HCH_3-*trans*); 54.6 (–*C*$(CH_3)_3$); 28.1 (–C(*C*H_3)$_3$); 15.9 (–CH=CH*C*H_3-*trans*); 12.6 (–CH=CH*C*H_3-*cis*).

4.3.8. (E,E,E)-N,N,N-tri(1-propenyl)amine

MS (70 eV) *m*/*e* (int[%]): 137 (100) M^+; 122 (27); 108 (11); 94 (7); 68 (23); 39 (44). ^{1}H NMR ($CDCl_3$): δ = 6.07 (dq, 3H, J = 13.2, 1.2 Hz, –C*H*=$CHCH_3$), 4.82 (dq, 3H, J = 13.2, 6.9 Hz, –CH=C*H*CH_3), 1.80 (dd, 9H, J = 6.3, 1.2 Hz, –CH=C*H*CH_3). ^{13}C NMR ($CDCl_3$): δ = 131.9 (–*C*H=$CHCH_3$); 104.4 (–CH=*C*HCH_3); 15.2 (–CH=CH*C*H_3).

4.3.9. (E,E,E,E)-N,N,N′,N′-tetra(1-propenyl)-1,2-ethandiamine

MS (70 eV) *m*/*e* (int[%]): 220 (21) M^+; 191 (72); 164 (100); 151 (43); 148 (12); 136 (8); 122 (26); 110 (54); 94 (18), 82 (13); 68 (28); 55 (10). ^{1}H NMR ($CDCl_3$): δ = 5.92 (dq, 4H, J = 13.8, 1.5 Hz, –C*H*=$CHCH_3$), 4.53 (dq, 4H, J = 13.8, 7.2 Hz, –CH=C*H*CH_3), 3.31 (s, 4H, –C*H*$_2$–), 1.66 (dd, 12H, J = 7.2, 1.5 Hz, –CH=CHC*H*$_3$). ^{13}C NMR (C_6D_6): δ = 126.3 (–*C*H=$CHCH_3$); 102.7 (–CH=*C*HCH_3); 54.4 (–CH_2–); 14.8 (–CH=CH*C*H_3).

4.3.10. (E)-N,N-bis(trimethylsilyl)-N-(1-propenyl)amine

MS (70 eV) *m*/*e* (int[%]): 201 (23) M^+; 186 (100); 172 (48); 132 (3); 128 (6); 112 (23); 73 (15); 59 (4); 55 (1); 45 (50). ^{1}H NMR ($CDCl_3$): δ = 5.75 (dq, 1H, J = 13.2, 1.2 Hz, –C*H*=$CHCH_3$), 4.88 (dq, 1H, J = 13.2, 6.3 Hz, –CH=C*H*CH_3), 1.48 (dd, 3H, J = 6.3, 1.2 Hz, –CH=CHC*H*$_3$), 0.06 (s, 1H, –Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ = 134.6 (–*C*H=$CHCH_3$); 116.2 (–CH=*C*HCH_3); 15.1 (–CH=CH*C*H_3), 2.08 (Si(*C*H_3)$_3$).*(Z)-N,N-bis(trimethylsilyl)-N-(1-propenyl)amine*. MS (70 eV) *m*/*e* (int[%]): 201 (24) M^+; 186 (100); 172 (68); 128 (9); 112 (36); 86 (5); 73 (60); 59 (14); 55 (2); 45 (17). ^{1}H NMR($CDCl_3$): δ = 5.71 (dq, 1H, J = 7.2, 1.2 Hz, –C*H*=$CHCH_3$), 5.08 (dq, 1H, J = 7.2, 7.2 Hz, –CH=C*H*CH_3), 1.46 (dd, 3H, J = 7.2, 1.2 Hz, –CH=CHC*H*$_3$), 0.03 (s, 1H, –Si(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6): δ = 132.4 (–*C*H=$CHCH_3$); 122.0 (–CH=*C*HCH_3); 12.2 (–CH=CH*C*H_3), 1.6 (–Si(*C*H_3)$_3$).

4.3.11. N-methyl-N-(3-trimethylsilyl-1-propenyl)aniline

MS (70 eV) *m*/*e* (int[%]): 219 (100) M^+; 204 (11); 189 (7); 146 (38); 143 (8); 120 (30); 73 (7); 59 (4); 40 (7). ^{1}H NMR ($CDCl_3$): 5 = 7.45 (ddd, 2H, J_{2-3} = J_{5-6} = 7.8, J_{3-4} = J_{4-5} = 7.2, J_{3-5} = 1.5 Hz, $H_{3\text{-arom}}$ and $H_{5\text{-arom}}$), 7.10 (dd, 2H, J_{2-3} = J_{5-6} = 7.8 Hz, J_{2-4} = J_{4-6} < 0.9 Hz, $H_{2\text{-arom}}$ and $H_{6\text{-arom}}$), 7.02 (dd, 1H, J_{3-4} = J_{4-5} = 7.2 Hz, J_{2-4} = J_{4-6} < 0.9 Hz, $H_{4\text{-arom}}$), 6.63 (dq, 1H, J = 13.5, 1.2 Hz, –C*H*=$CHCH_2$–), 4.75 (dq, 1H, J = 13.5, 8.1 Hz, –CH=C*H*CH_2–), 3.29 (s, 3H, –C*H*$_3$), 1.61 (dd, 2H, J = 6.6, 1.2 Hz, –CH=CH*C*H_2–), 0.04 (s, 9H, –Si$(CH_3)_3$). ^{13}C NMR (CDCl3): δ = 140.4 ($C_{1\text{-arom}}$); 129.7 ($C_{3\text{-arom}}$ and $C_{5\text{-arom}}$); 128.7 ($C_{2\text{-arom}}$ and $C_{6\text{-arom}}$); 128.3 ($C_{4\text{-arom}}$); 126.9 (–*C*H=$CHCH_2$–); 111.9 (–CH=*C*HCH_2–); 39.2 (–*C*H_3); 19.4 (–CH=CH*C*H_2–); –2.13 (–Si(*C*H_3)$_3$).

4.4. Spectroscopic measurements

^{1}H and ^{13}C NMR spectra were measured on a Varian Unity 300 MHz spectrometer. GC–MS were run on: (a) a Varian 3300 gas chromatograph equipped with a 30 m long DB 1701 fused silica capillary column and a Finnigan MAT 800 AT ion trap detector; (b) aVarian Saturn 2100T gas chromatograph equipped with a 30 m long DB-5 capillary column and TCD detector; (c) Thermo Finnigan equipped with a 30 m long MDN 5S column and Mass Detector (EI, 70 eV). HPLC-MS spectra were recorded on HPLC-MS Waters Integrity Systems with a Thermabeam Mass Detector (EI, 70 eV), Photodiode Array detector on a cartridge column; methanol–water mixture (70:25; flow 0.25 ml/min) used as the solvent.

4.5. Theoretical calculations

All calculations were performed using GAMESS [38] and its PC version: PC GAMESS [39], running on a two-processor Linux server. MOLDEN [40] was used for the construction of *Z*-matrices visualization of the results. Geometries were optimized using either delocalized internal [41] or Cartesian coordinates. Hessian calculations were performed for each stationary point found, to ensure that it is a local minimum. In order to select the most appropriate method for geometry optimization, a series of calculations (for *N*,*N*-dimethylallylamine) was carried out, on various levels of theory (PM3 [42,43], RHF/6-31G(d,p) [44–47], MP2/6-31G(d,p) [48], MP2/6-311G(2df,2p) [49]). The geometry changed significantly upon increasing the level of theory from PM3 to RHF/6-31G(d,p), electron correlation on the MP2 level was found to be important, but an expansion of the basis to 6-311G(2df,2p) did not produce any important difference that would justify much higher computational costs associated with this basis set (see Table 2).

Therefore MP2/6-31G(d,p) was chosen for the rest of optimizations. C_1-symmetric geometries were found to be more stable than C_s (the latter were transition states between conformations). The geometry and electronic structure of *N*,*N*-dimethylallylamine has already been investigated computationally [50] but the author published neither the optimized structure nor the shapes of the orbitals, therefore we could not use his results. In order to predict how the allyl compounds and their propenyl isomers are coordinated by the metal atom, we have analyzed the shapes of the RHF canonical orbitals. It was assumed that these regions of the molecule where HOMO-1 and HOMO are significantly nonzero may participate in donor bonding with the metal, and those where LUMO and LUMO+1 are localized are involved in back-bonding.

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