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Synthesis of *N*-Arylpyrroles, Hetero-Diels−Alder Adducts, and Allylic Amines by Reaction of Unfunctionalized Dienes with Nitroarenes and Carbon Monoxide, Catalyzed by $Ru(CO)_3$(Ar-BIAN)

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The reaction between an unfunctionalized conjugated diene and a nitroarene under CO pressure, catalyzed by $Ru_3(CO)_{12}$/Ar-BIAN (Ar-BIAN = bis(arylimino)acenaphthene), affords the corresponding allylic amine (**1**), the hetero-Diels−Alder adduct (oxazine) (**2**), and the *N*-arylpyrrole (**3**) in different ratios depending on the experimental conditions. The synthesis of the allylic amine involves an intermolecular catalytic C−H functionalization by a transition metal complex. Compounds **1** and **2** are primary products of the reaction, whereas **3** derives from a following reaction of **2**. By running the reaction at 120 °C, the decomposition of **2** to **3** is completely suppressed, allowing for the isolation of **2** in good yields. On the contrary, at 200 °C **2** is completely transformed into **3** during the reaction. The selectivity in allylic amine is somewhat sensitive to the experimental conditions and always ranges between 15 and 25%. Electron-withdrawing substituents on the nitroarene give better results, but electron-donating ones slow the reaction and give lower selectivities. Steric hindrance on the nitroarene strongly retards the reaction, but use of 2-methylnitrobenzene allowed for the isolation and X-ray structural characterization of a resting state of the catalytic system, $\overline{\mathrm{Ru[N(\mathit{o}\text{-}CH_3C_6H_4)C(O)N(\mathit{o}\text{-}CH_3C_6H_4)C}}\mathrm{(O)](CO)_2(Ph\text{-}BIAN)}$ (**9**).

Introduction

The synthesis of allylic amines[1] and of pyrroles[2] has been the focus of much attention in recent years. The synthesis of hetero-Diels−Alder adducts derived from nitrosoarenes as dienophiles (oxazines) has also been investigated, since these products have pharmacological activity themselves or can be easily transformed into other products.[3] However, their usual synthesis requires the intermediate isolation of nitroso compounds, which is problematic, although an approach has also been reported in which oxidation of an aromatic amine in the presence of a diene results in the trapping of the intermediately formed nitrosoarene to give the hetero-Diels−Alder adducts in one pot.[4,5] As far as allylic amines are considered as products, most reported synthetic procedures require the availability of prefunctionalized starting materials, such as an allyl acetate, or require the use of unfavorable materials.[1] In both cases the reactions produce salts as byproducts. This latter feature is becoming increasingly unacceptable for industrial processes. Transition metal mediated intermolecular activation and functionalization of C−H bonds avoids this problem. Several synthetic approaches are available for the synthesis of pyrroles, but few of them are applicable to *N*-arylpyrroles.[2] Moreover, most synthetic methods give the best results for pyrroles bearing one or two substituents in the 2 and 5 positions. On the contrary, our procedure is best suited for pyrroles that are only substituted in the 3 and 4 positions.

We have recently reported[6,7] a new synthetic way to produce allylic amines, employing a simple unactivated

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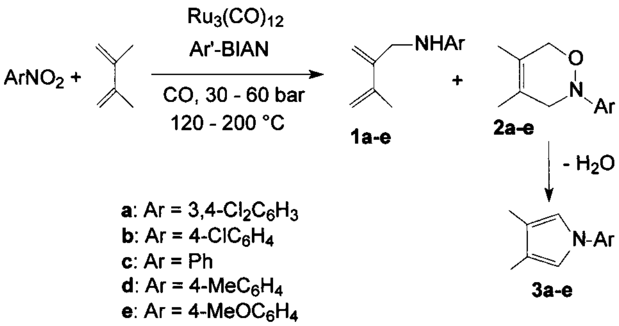
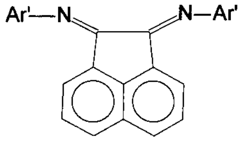
10.1021/om010076j CCC: $20.00

Scheme 1



olefin and an aromatic nitro compound as the aminating reagent, under reducing conditions (CO pressure). Nicholas and co-workers have reported on a similar system.[8,9] During our previous work, we briefly investigated the use of 2,3-dimethyl-1,3-butadiene in place of simple olefins, to detect whether hetero-Diels−Alder adducts were formed from the intermediately formed nitrosoarene and the diene. Indeed, we detected the formation of the expected adduct, but accompanied by the allylic amine and by an *N*-arylpyrrole. It was shown that the hetero-Diels−Alder adduct and the allylic amine are independent primary products of the reaction, but the pyrrole derives from further reaction of the adduct. The formation of none of the products occurs via the aniline corresponding to the nitroarene, which is also formed as a byproduct. Since the use of the diene had only been prompted by the need to obtain mechanistic information on the system, the possible synthetic application of this reaction was not investigated at the time. We have now investigated the use of several nitroarenes and dienes in this reaction, and the results are reported herein (Scheme 1).

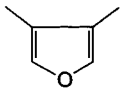


Ar'-BIAN

(Ar' = Ph, 4-ClC_6H_4, 3,5-$Cl_2C_6H_3$, 4-$MeOC_6H_4$)

Results and Discussion

Influence of the Experimental Conditions When Using Nitrobenzene and 2,3-Dimethylbutadiene as Substrates. In our previous paper, we reported that performing the catalytic reaction between nitrobenzene and 2,3-dimethylbutadiene in the presence of $Ru_3(CO)_{12}$/Ph-BIAN in toluene at 160 °C and under 40 bar CO afforded a mixture of allylic amine **1c**, hetero-Diels−Alder adduct (2-phenyl-4,5-dimethyl-3,6-dihydro-2*H*-[1,2]-oxazine) **2c**, and *N*-phenyl-3,4-dimethylpyrrole **3c**. The formation of pyrroles by decomposition of hetero-Diels−Alder adducts is not unprecedented. The same reaction is known to occur by photochemical activation[10] and, at least in some cases, by thermal activation.[3a] Moreover, it has been reported that $[Rh(COD)Cl]_2$ catalyzes the same reaction under CO pressure.[11] On the other hand, we never detected the product of CO insertion into the ring, which is known to be formed in the presence of $Co_2(CO)_8$.[11] The analysis of the amount of **2a** and **3a** by gas chromatography is only semiquantitative, since the hetero-Diels−Alder adduct partly decomposes to the pyrrole even during the analysis and the amount of decomposition varies with the concentration. The molar ratio (pyrrole + adduct)/allylic amine was close to 3 and did not vary appreciably when the reaction temperature was lowered to 80 °C, the pressure was changed in the range 20−50 bar, or the amount of 2,3-dimethylbutadiene was varied from 0.5 to 2 mL, although the nitrobenzene conversion increased along this last series (40, 60, 65%). We have now examined the use of different solvents and additives, and the results are reported in Tables 1 and 2.



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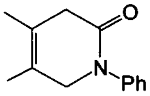

(5)

Aniline and diphenylurea are byproducts that are generally present in 8−15% yield and derive from deoxygenation and carbonylation reactions that do not involve the olefin. In some cases, we could also find evidence of the presence of trace amounts of the dimer of the olefin, of 3,4-dimethylfuran (**4**), and of 1-phenyl-4,5-dimethyl-3,6-dihydro-1*H*-pyridin-2-one (**5**). The latter is likely to derive from the Diels−Alder reaction between the diene and some phenylisocyanate formed as byproduct and normally trapped by aniline to give diphenylurea. The formation of furans during the photochemical decomposition of hetero-Diels−Alder adducts to pyrroles has been previously observed.[10] The hetero-Diels−Alder reaction between dienes and arylisocyanates also has precedents,[3a] even if in the present case it is not clear which role the metal plays in the formation of this product. Products **4** and **5** are formed in very low amounts and were only observed by GC−MS analysis of some fractions after chromatographic separation of the reaction mixtures. They could not be observed in the gas chromatograms of the crude mixtures.

As previously mentioned, the gas chromatographic analysis of **2c** and **3c** is only semiquantitative, but the sum of the selectivities for the two appears to be between 40 and 60% in all the experiments which gave good results for the allylamine, although the selectivity is lower for entry 6 in Table 1 and for the last three entries in Table 2. The selectivity in **1c** is also remarkably constant and close to 20%. Overall, the solvent does not play a relevant role. Hexane gave the fastest reactions, but the selectivity was slightly better in toluene. The addition of aniline to the reaction mixture (entry 5, Table 1) increases the amount of diphenylurea obtained, but does not alter the amount of **1c**. The

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Table 1. Influence of the Experimental Conditions on the Reaction between Nitrobenzene and 2,3-Dimethylbutadiene, Catalyzed by $Ru_3(CO)_{12}$/Ph-BIAN[a]

entry	solvent	*t*/h	nitrobenzene conv. %[b]	allylic amine select. %[c]	diphenylurea select. %[c]	aniline select. %[c]
1	toluene	4	72.6	20.3	7.4	9.6
2	THF	4	92.6	18.5	12.6	13.9
3	hexane	4	100	18.1	7.6	12.8
4	toluene	2	60.0	21.4	11.0	8.8
5[d]	toluene	2	71.3	18.0	23.6	12.2[e]
6[f]	toluene	2	33.1	6.3	33.4	14.8

[a] Experimental conditions: $Ru_3(CO)_{12}$ = 19.2 mg, 0.030 mmol, mol ratio $Ru_3(CO)_{12}$/Ph-BIAN/$PhNO_2$ = 1:3.75:100, T = 160 °C, P_{CO} = 40 bar, 2,3-dimethylbutadiene = 1 mL, solvent 9 mL. Both conversion and products amounts were measured by GC. The GC analysis of **2c** and **3c** is only semiquantitative, but the sum of their selectivities is approximately 40−60% for entries 1−5, although it is lower for entry 6. [b] Calculated with respect to the starting nitrobenzene. [c] Calculated with respect to the converted nitrobenzene. [d] Aniline (1.0 mmol) was also added to the reaction mixture. [e] Value referred to the amount of aniline found in excess with respect to the one initially charged. [f] 2,4,6-Trimethylbenzoic acid (0.45 mmol) was also added to the reaction mixture.

Table 2. Influence of the Ligand on the Reactions between Nitrobenzene and 2,3-Dimethylbutadiene Catalyzed by $Ru_3(CO)_{12}$[a]

ligand	nitrobenzene conv. %[b]	allylic amine select. %[c]	diphenylurea select. %[c]	aniline select. %[c]
Ph-BIAN	100	18.1	7.6	12.8
4-ClC_6H_4-BIAN	100	18.9	5.8	11.3
3,5-$Cl_2C_6H_3$-BIAN	100	21.2	4.0	8.8
4-$MeOC_6H_4$-BIAN	68.0	18.3	8.0	14.0
2,2′-biquinoline	16.2	9.7		10.8
none	7.3	5.7	5.8	30.2
acenaphthenequinone	59.9	13.0		18.2

[a] Experimental conditions: $Ru_3(CO)_{12}$ = 19.2 mg, 0.030 mmol, mol ratio $Ru_3(CO)_{12}$/ligand/$PhNO_2$ = 1:3.75:100, 2,3-dimethylbutadiene = 1 mL, T = 160 °C, P_{CO} = 40 bar, in hexane (9 mL), for 4 h. Both conversion and products amounts were measured by GC. The GC analysis of **2c** and **3c** is only semiquantitative, but the sum of their selectivities is approximately 50−60% in the reactions with BIAN ligands, but is lower in the other cases. [b] Calculated with respect to the initial nitrobenzene. [c] Calculated with respect to the converted nitrobenzene.

addition of a noncoordinating weak acid (2,4,6-trimethylbenzoic acid), on the other hand, has a markedly negative effect on the reaction (entry 6).

The effect of different ligands was also explored (Table 2). The ligands Ph-BIAN, *p*-ClC_6H_4-BIAN, and 3,5-$Cl_2C_6H_3$-BIAN gave almost indistinguishable results, whereas the presence of a methoxy group has a negative effect on the reaction. By analogy with the results previously reported by us when examining the reactions with cyclohexene,[7] the most probable explanation for the observed effect is that *p*-$MeOC_6H_4$-BIAN is too basic a ligand to efficiently coordinate to a Ru^0 complex and is easily displaced by CO. A ligand such as 2,2′-biquinoline, which has been calculated to have HOMO−LUMO energies close to the ones of BIAN ligands,[12] gave much worse results in terms of both conversion and selectivity. Ligands such as phenanthroline and phosphines had already been shown not to be suitable for reactions of this kind.[6,7] In the absence of any ligand, the conversion is low and the main product is aniline, analogously to what is found for simple olefins. Interestingly, acenaphthenequinone, the starting material for the synthesis of BIAN ligands, is also a promoter for the reaction, even if less efficient than the BIAN ligands themselves. It is possible that the quinone generates Ph-BIAN in situ by reaction with the formed aniline, although it is not possible to exclude coordination of the quinone as such. A similar situation has been earlier observed by ourselves in the related reduction of nitrobenzene to aniline by CO/H_2O again catalyzed by $Ru_3(CO)_{12}$/Ar-BIAN.[13]

Use of Different Nitroarenes and Dienes. The scope and limits of the reaction in Scheme 1 were examined by using a series of different nitroarenes, with 2,3-dimethylbutadiene as the reference diene, employing ^1H NMR spectroscopy to quantify products **1**, **2**, and **3** and gas chromatography for the analysis of the nitroarene and aniline.

As can be seen from the results reported in Table 3, the best temperature to obtain the allylic amine is 160 °C, in accord with the results obtained for simple olefins, but the selectivity in this product is always low and a mixture of **2** and **3** is present. However, by working at 120 °C the decomposition of **2** into **3** is completely avoided and moderate to good selectivities into the hetero-Diels−Alder adduct can be obtained. On the contrary, at 200 °C **2** is completely transformed into **3** during the reaction. Electron-withdrawing substituents on the nitroarene give results similar to the ones obtained with nitrobenzene, but electron-donating ones slow the reaction and lower the selectivity in allylamine and **2** + **3**. With *p*-$MeOC_6H_4NO_2$ a complete conversion was not achieved after 6 h even when the catalytic ratio was halved. Moreover, in this case the main product obtained was the diarylurea. The reason for the change in selectivity on passing from electron-withdrawing substituents to electron-donating ones can be explained by the reaction mechanism shown in Scheme 2, which is derived from the previously reported data.[7] The key point is the formation of a nitrosoarene complex, in which an olefin and a CO group are also present. Indeed, in the coupling with the olefin, the nitrosoarene acts as

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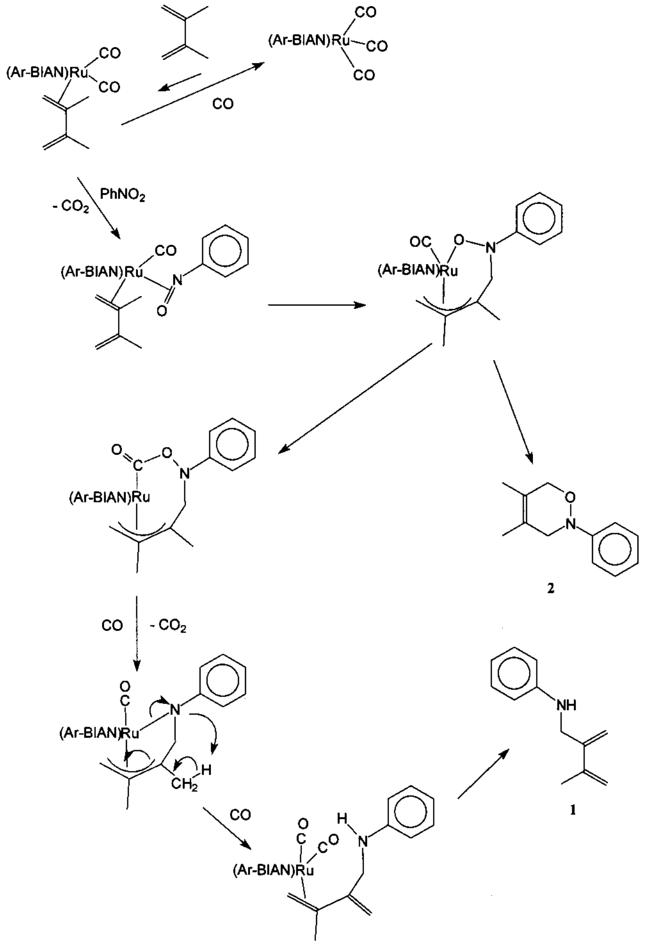
Table 3. Reactions between 2,3-Dimethylbutadiene and Different Nitroarenes, Catalyzed by $Ru_3(CO)_{12}$/Ph-BIAN[a]

nitroarene	T/°C	t/h	$ArNO_2$ conv. %[b]	allylic amine (**1**) select. %[c]	adduct (**2**) select. %[c]	pyrrole (**3**) select. %[c]
3,4-$Cl_2C_6H_3NO_2$	120	10	77.7	16.4	51.8	0
3,4-$Cl_2C_6H_3NO_2$	160	6	100	20.1	25.9	17.7
3,4-$Cl_2C_6H_3NO_2$	200	6	100	18.2	0	43.1
4-$ClC_6H_4NO_2$	120	10	78.5	9.3	42.6	0
4-$ClC_6H_4NO_2$	160	6	100	12.8	15.2	31.6
4-$ClC_6H_4NO_2$	200	6	100	12.9	0	42.3
$PhNO_2$	120	10	78.3	15.1	57.8	1.9
$PhNO_2$	160	6	100	15.2	13.7	29.6
$PhNO_2$	200	6	100	12.9	0	56.4
4-$CH_3C_6H_4NO_2$	160	6	100	11.2	24.4	14.1
4-$CH_3OC_6H_4NO_2$[d]	160	6	91.5	9.0	22.5	15.2

[a] Experimental conditions: $Ru_3(CO)_{12}$ = 19.2 mg, 0.030 mmol, mol ratio nitroarene/$Ru_3(CO)_{12}$ = 50, mol ratio $Ru_3(CO)_{12}$/Ph-BIAN = 1:4, 2,3-dimethylbutadiene = 1 mL, 40 bar of CO, in hexane (9 mL). Nitroarenes conversions were measured by GC; products amounts were measured by ^1H NMR, using 2,4-dinitrotoluene as an internal standard. The main byproducts of the reactions are the nitroarene-derived diarylureas and anilines. [b] Calculated with respect to the starting nitroarene. [c] Calculated with respect to the converted nitroarene. [d] Mol ratio nitroarene/$Ru_3(CO)_{12}$ = 25.

Scheme 2



an electrophile and these kinds of couplings are known to be accelerated by electron-withdrawing groups on the aromatic ring.[14] Alternatively the nitrosoarene may attack the coordinated CO, a reaction that has been observed for the related $Ru(CO)_2(DPPE)(\eta^2\text{-}ArNO)$ complexes[15,16] and is the only one occurring when no olefin is present. This reaction will eventually lead to byproducts. In this case the nitrosoarene acts a nucleophile and the reaction is retarded by the same groups on the arene that accelerate the reactions with olefins.

The rate of conversion of **2** into **3** appears to be lowest for Ar = Ph and to be increased both by electron-withdrawing and electron-donating substituents on the nitroarene ring.

Use of 4-$FC_6H_4NO_2$ gave a difficult to separate mixture of products. It appears that the carbon−fluorine bond may also be attacked under these conditions.

Use of 2-methylnitrobenzene to test the effect of steric hindrance gave a slow reaction and only trace amounts of olefin-containing products, ditolylurea, being formed in large amounts. However, the use of this nitroarene allowed the isolation and X-ray structural characterization of a resting state of the catalytic system, as better detailed in the following.

The use of different olefins was investigated by using *p*-chloronitrobenzene as a reference substrate. Use of 1,4-diphenylbutadiene gave very low conversions and only trace amounts of hetero-Diels−Alder adduct and pyrrole, even when the reaction was conducted at 200 °C, which is at least partly due to a reversibility in the formation of the hetero-Diels−Alder adduct at high temperature. We directly observed this reversibility by heating the adduct obtained by reaction of nitrosobenzene with 1,4-diphenylbutadiene. Cyclohexadiene also gave poor selectivities, but good results were obtained with isoprene (Table 4).

Two adducts are possible from the reaction between a nitroarene and isoprene, but only **7A** has been reported to be obtained by reaction of isoprene with *p*-chloronitrosobenzene.[17] In our reaction, we also could clearly identify only one isomer for **7**, which was identified as **7a** by comparison of its ^1H NMR spectrum with the one reported in the literature for this compound. However, it should be mentioned that in the ^1H NMR spectrum of the crude reaction mixture some low-intensity signals are present, which could not be attributed to any known compound and which are close to the ones of **7a**. Thus they could be due to a small amount (4−5% with respect to **7a**) of **7b**. Attempts to

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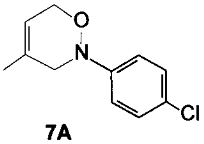
Table 4. Reactions between Isoprene and $4\text{-}ClC_6H_4NO_2$, Catalyzed by $Ru_3(CO)_{12}$/Ph-BIAN[a]

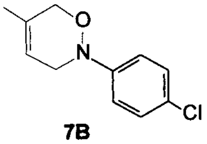
$Ru_3(CO)_{12}$ amount/mmol	Ph-BIAN/$Ru_3(CO)_{12}$ mol ratio	$4\text{-}ClC_6H_4NO_2$/$Ru_3(CO)_{12}$ mol ratio	isoprene/mL	solvent (mL)	*T*/°C	*t*/h	$4\text{-}ClC_6H_4NO_2$ conv. %[b,c]	allylic amine (**6**) select. %[d]	adduct (**7**) select. %[d,e]	pyrrole (**8**) select. %[d,e]	$4\text{-}ClC_6H_4NH_2$ select. %[c,d]
1.0×10^{-2}	4.5	200	0.5	toluene (9.5)	140	1	29.3	25.1[c]	*f*	*f*	24
1.0×10^{-2}	4.5	200	1	toluene (9)	140	1	25.5	28.5[c]	*f*	*f*	19.8
1.0×10^{-2}	4.5	200	2	toluene (8)	140	1	24.9	32.4[c]	*f*	*f*	22
1.0×10^{-2}	4.5	200	4	toluene (6)	140	1	34.7	23.2[c]	*f*	*f*	18.8
1.0×10^{-2}	4.5	200	10		140	1	38	24.6[c]	*f*	*f*	9.4
3.0×10^{-2}	4	50	1	toluene (9)	120	10	52.6	11.3[e]	19.4	0	7
3.0×10^{-2}	4	50	5	toluene (5)	120	10	55.7	17.3[e]	28	0	11.1
3.0×10^{-2}	4	50	10		120	10	49.6	16.5[e]	25.8	0	9.3
3.0×10^{-2}	4	50	1	hexane (9)	120	10	63.2	14.3[e]	28.2	0	10.6

[a] Experimental conditions: 40 bar of CO. The main byproduct of the reactions is *N*,*N*′-(p-$ClC_6H_4NH)_2CO$. [b] Calculated with respect to the starting nitroarene. [c] Measured by GC. [d] Calculated with respect to the converted nitroarene. [e] Measured by ^1H NMR, using 2,4-dinitrotoluene as an internal standard. [f] Not determined.

isolate this small amount of substance to better characterize it failed.



7A



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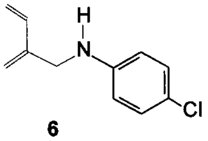

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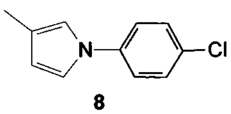

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The effect of the concentration of isoprene in the reaction mixture was examined by changing its amount from 0.5 to 10 mL, the complement to 10 mL being toluene. The conversion changed only little in a series conducted at 140 °C, a minimum being observed at medium isoprene concentrations. At 120 °C and at a longer reaction time (10 h instead of 1 h) the differences in conversion are even smaller and close to the experimental uncertainty. This is in contrast with the results previously obtained with cyclohexene,[6,7] for which a first-order dependence of the rate on the olefin concentration had been found, and even with what was observed for 2,3-dimethylbutadiene[7] (see above), for which an increase in conversion on passing from 0.5 to 2 mL has been observed, although the increase is not linear. The selectivity in allylic amine (**6**) shows a maximum at medium isoprene concentrations in both series, and the same is true (at least for the one at 120 °C) for the selectivity in **7**. Although the selectivities in nitrogen-containing products vary little in these two series, it should be noted that the amounts of dimeric products of isoprene increase very much on increasing isoprene concentration. Dimers are barely detectable by GC at 0.5 or 1 mL of isoprene (10 mL total volume), but become the most abundant product when the neat diolefin is used as solvent. Similarly to previous observations, use of hexane as solvent in place of toluene gave a higher conversion, but, in this case, a higher selectivity was also observed.

Analogously to what was found for 2,3-dimethylbutadiene, no pyrrole is formed at 120 °C, but at 200 °C, conversion of **7a** into *N*-(*p*-chlorophenyl)-3-methylpyrrole (**8**) was quantitative. At this high temperature, the use of a 1:1 volume ratio of isoprene/toluene as solvent caused the formation of such a large amount of dimeric products that the reaction could not be analyzed by NMR.

Separation of the Organic Products. It was not the aim of this work to improve the separation of the organic products, and we usually employed column chromatography to isolate pure samples of them. However, the following improved separation techniques are worth noting. Allylic amines can be separated by extraction with aqueous HCl together with the corresponding aniline. At least in the case of aniline, a following chromatographic separation can be avoided by heating at 80 °C under vacuum (10^{-2} Torr) the oil obtained after neutralization and back extraction. This procedure allows for the selective evaporation of aniline, leaving the allylamine contaminated by less than 0.1% aniline. *N*-Phenyl-3,4-dimethylpyrrole can be similarly sublimed at 60 °C under vacuum from the fraction that has not been extracted with HCl. Chromatographic purification of hetero-Diels−Alder adducts over silica notoriously affords poor isolated yields because of decomposition of the compound during the separation.[4a] We have now found that if neutral alumina is employed instead of silica, the adducts are isolated with negligible losses. Adducts **3** show retention factors very close to those of the corresponding nitroarenes, so separation is best conducted on reaction mixtures in which conversion of the nitroarene is complete.

Deactivation of the Catalytic System. From a comparison among the data reported in the Tables, it is clear that reactions conducted with 2,3-dimethylbutadiene or isoprene proceed at comparable rates when the reaction time is 1 h, but reactions conducted for 10 h are markedly slower for the second olefin. The reason for this effect is to be found in the formation of complexes of the type $Ru(CO)_3(\eta^4\text{-diene})$ (diene = 2,3-dimethylbutadiene or isoprene). We have already observed the formation of the complex $Ru(CO)_3(\eta^4\text{-}2,3\text{-dimethylbutadiene})$[18] by high-pressure IR spectroscopy of solutions containing both $Ru(CO)_3$(Ph-BIAN) and 2,3-dimethylbutadiene, but its formation was very slow under typical reaction conditions.[7] We have now found that formation of the corresponding complex $Ru(CO)_3(\eta^4\text{-isoprene})$ is much faster under the reaction conditions. Figure 1 shows two IR spectra recorded after two reactions performed between $Ru_3(CO)_{12}$, Ph-BIAN, and respectively 2,3-dimethylbutadiene and isoprene under

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[18] Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta* **1974**, *8*, 71.

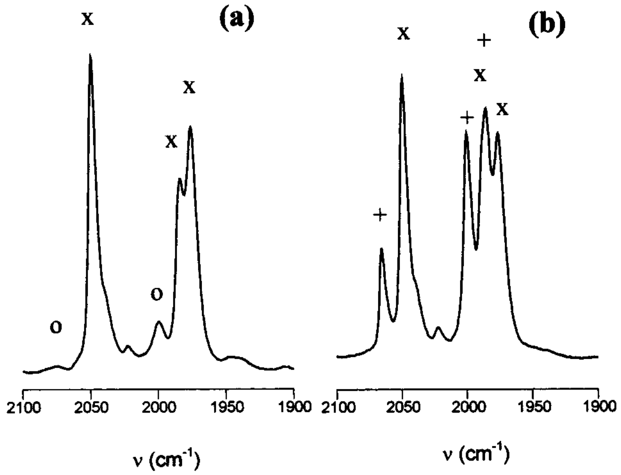

Figure 1. IR spectra of the reaction mixtures of $Ru_3(CO)_{12}$ (0.030 mmol), Ph-BIAN (0.120 mmol), and 2,3-dimethylbutadiene (a) (1 mL) or isoprene (b) (1 mL) in hexane (9 mL) after 5 h at 120 °C and under 40 bar of CO. x = $Ru(CO)_3$(Ph-BIAN), o = $Ru(CO)_3(\eta^4$-2,3-dimethylbutadiene), + = $Ru(CO)_3(\eta^4$-isoprene). The absorption at 1987 cm^{-1} of $Ru(CO)_3(\eta^4$-2,3-dimethylbutadiene) is hidden below one of the more intense absorptions of $Ru(CO)_3$(Ph-BIAN). The weak absorption at 2030 cm^{-1} is probably due to $Ru(CO)_5$.

typical catalytic conditions (120 °C, 40 bar CO), but in the absence of nitroarenes. After 5 h, the solution containing 2,3-dimethylbutadiene contains $Ru(CO)_3$(Ph-BIAN) as the largely dominant complex, only very small amounts of $Ru(CO)_3(\eta^4$-2,3-dimethylbutadiene) being detected (Figure 1a). On the contrary, in the case of isoprene, $Ru(CO)_3(\eta^4$-isoprene) is already present in large amounts in solution (Figure 1b). The complex $Ru(CO)_3(\eta^4$-isoprene) is much less reactive than $Ru(CO)_3$(Ph-BIAN) with respect to nitroarenes, as proved by the following experiment. A mixture containing comparable amounts of the two complexes was obtained by reacting $Ru_3(CO)_{12}$ and Ph-BIAN in neat isoprene at 160 °C and under 40 bar CO for 2 h. To this mixture was added nitrobenzene at room temperature (and under a dinitrogen atmosphere). The IR absorptions due to $Ru(CO)_3$(Ph-BIAN) completely disappeared in less than 3 min (time needed to withdraw a sample and record an IR spectrum), but the intensity of the ones due to $Ru(CO)_3(\eta^4$-isoprene) was unaltered for at least 6 h.

It should also be noted that when monoolefins are employed as substrates, no olefinic complex is observed, but $Ru(CO)_5$ is slowly formed instead.[7] Under the present conditions, formation of the diolefin complex appears to be favored with respect to that of the pentacarbonyl complex, and only very small amounts of the latter are observable under any condition (for example see Figure 1).

Identification of a Resting State of the Catalytic System. As previously mentioned, use of 2-methylnitrobenzene afforded only very small yields of the desired products; however after a reaction run employing this nitroarene, a ruthenium complex $Ru[N(o\text{-}CH_3C_6H_4)C(O)N(o\text{-}CH_3C_6H_4)C(O)](CO)_2$(Ph-BIAN) (**9**) precipitated from the solution as orange-brown crystals, some of which were suitable for X-ray diffraction (see later).

Compound **9** can be more efficiently obtained by performing a reaction under typical catalytic conditions, but in hexane and in the absence of the diene, also employing larger amounts of $Ru_3(CO)_{12}$ and Ph-BIAN. In this way the coproduction of ditolylurea is minimized. When a pure sample of **9** obtained in this way was subjected to catalytic conditions (200 °C, 40 bar CO, in the presence of 2,3-dimethylbutadiene, but in the absence of nitroarenes), only ditolylurea and no pyrrole, oxazine, or allylic amine could be detected among the products. However, when **9** was employed as catalyst in a reaction between 2,3-dimethylbutadiene and 3,4-dichloronitrobenzene, the usual products derived from the chlorinated nitroarene were observed. The conversion was lower than usual (51.4 instead of 100%), but the selectivities were comparable to the ones obtained when using $Ru_3(CO)_{12}$/Ph-BIAN. Thus it is clear that although **9** is not a productive intermediate in the synthesis of **1**, **2**, or **3** (although it is an intermediate in the formation of diarylurea), it can reenter the catalytic cycle under the reaction conditions and is better considered as a resting state of the catalyst, rather than a deactivation product.

The IR spectrum of the complex (in THF) shows bands at 2038 (vs) and 1973 (s) cm^{-1} due to the two CO groups coordinated to ruthenium. Bands falling at very close positions were observed in several instances even with other nitroarenes, although the corresponding complexes could not be isolated. Thus the formation of complexes analogous to **9** appears to be general.

We point out that the main resting state of the catalytic system, as previously observed by high-pressure IR spectroscopy,[7] is $Ru(CO)_3$(Ar-BIAN). This is in equilibrium with the real catalytically active species $Ru(CO)_2(\eta^2$-olefin)(Ar-BIAN). Formation of **9** is not a desired reaction, but does not lead to irreversible deactivation of the catalyst. On the other hand, the formation of $Ru(CO)_3(\eta^4$-diolefin) does not appear to be reversible and corresponds to a true deactivation of the catalytic system.

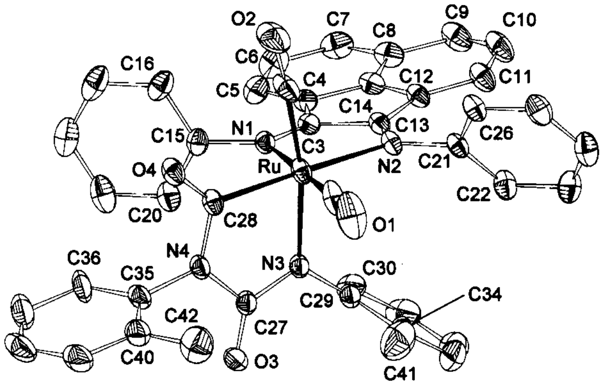

Figure 2. ORTEP drawing (ellipsoids at 30% probability level) and adopted numbering scheme of $Ru[N(o\text{-}CH_3C_6H_4)C(O)N(o\text{-}CH_3C_6H_4)C(O)](CO)_2$(Ph-BIAN) (**9**). Hydrogen atoms were omitted for clarity.

Description of the Structure of $Ru[N(o\text{-}CH_3C_6H_4)C(O)N(o\text{-}CH_3C_6H_4)C(O)](CO)_2$(Ph-BIAN) (9). Crystals of **9** consist of neutral molecules held together by normal van der Waals contacts. Figure 2 shows the molecular structure of **9** with a labeling scheme, while in Table 5 significant bond parameters are collected. Compound **9**

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $\overline{\mathrm{Ru[N(}o\mathrm{\text{-}CH_3C_6H_4)C(O)N(}o\mathrm{\text{-}CH_3C_6H_4)C(O)]}}$-(CO)$_2$(Ph-BIAN) (9)

Ru−C(1)	1.850(6)
Ru−C(2)	1.870(6)
Ru−C(28)	2.027(4)
Ru−N(1)	2.133(3)
Ru−N(2)	2.225(3)
Ru−N(3)	2.080(3)
O(3)−C(27)	1.218(5)
O(4)−C(28)	1.218(5)
N(1)−C(3)	1.299(5)
N(2)−C(13)	1.287(5)
N(3)−C(27)	1.350(5)
N(4)−C(27)	1.422(5)
N(4)−C(28)	1.396(5)
C(3)−C(13)	1.498(6)
C(1)−Ru−C(2)	89.8(3)
C(1)−Ru−N(1)	178.8(2)
C(2)−Ru−N(1)	91.3(2)
C(2)−Ru−N(2)	94.4(2)
C(2)−Ru−N(3)	169.4(2)
N(1)−Ru−N(2)	75.9(1)
C(28)−Ru−N(3)	79.5(2)
C(27)−N(3)−C(29)	118.3(3)
C(27)−N(3)−Ru	116.5(3)
C(29)−N(3)−Ru	125.1(2)
C(27)−N(4)−C(28)	120.2(3)
C(27)−N(4)−C(35)	120.3(4)
C(28)−N(4)−C(35)	119.5(3)
O(3)−C(27)−N(3)	127.8(4)
O(3)−C(27)−N(4)	120.4(4)
N(3)−C(27)−N(4)	111.8(4)
O(4)−C(28)−N(4)	119.7(4)
O(4)−C(28)−Ru	128.4(4)
N(4)−C(28)−Ru	111.9(3)

represents the first example of a structurally characterized Ru complex containing a bis(arylimino)acenaphthene ligand; previous examples of complexes containing this ligand, and fully characterized by means of X-ray diffraction, comprise only square-planar palladium centers. The ruthenium center is octahedrically coordinated by two cis CO ligands, two N donor atoms from the Ph-BIAN ligand, and a chelating ligand that can be viewed as the head-to-tail coupling product of two *o*-tolylisocyanate molecules. The octahedral environment is distorted owing to the presence of the two chelating ligands whose bite angles are significantly smaller than 90° (N(1)−Ru−N(2) 75.9(1)°, C(28)−Ru−N(3) 79.5(2)°). Moreover the CO(2) ligand is slightly bent away from the Ph-BIAN moiety, giving rise to a C(2)−Ru−N(3) bond angle of 169.4(2)°. Comparison of the Ru−N$_{\mathrm{BIAN}}$ bond distances (Ru−N(1) 2.133(3), Ru−N(2) 2.225(3) Å) with other ruthenium−bisimine complexes reveals close similarity (Ru−N in the range 1.99−2.15 Å). The significant difference between Ru−N(1) and Ru−N(2) could arise from different trans-influence of the carbonyl CO(1) and carbamoyl moiety; in a Pd complex with *o*-phenanthroline and a carbamoyl ligand[19] akin to the present one (vide infra) the Pd−phenanthroline bond trans to the carbamoyl C atom is longer by ca. 0.1 Å with respect to the other one (Pd−N(2) 2.169(3), Pd−N(1) 2.062(4) Å). Nevertheless, in **9** steric crowding could also be an important factor for determining the Ru−N(2) bond length, owing to closeness of the phenyl groups bound to N(2) and N(3) (H(22)···C(32) ca. 3.09 Å).

The suitable catalytic properties of bis(arylimino)acenaphthene complexes arise from the presence of two exocyclic chelating imine groups coupled with rigidity of the acenaphthene backbone, thus preventing rotation about the imine C−C bond. To analyze the stereochemical features of the BIAN moiety in **9**, its geometric parameters can be compared with those of the free ligand[12] and the Pd derivatives containing Ar-BIAN ligands.[12,20−22] First of all, the acenaphthene unit in **9** exhibits a bonding geometry coherent with a classical resonance picture giving rise to higher bond order for the C(4)−C(5), C(6)−C(7), C(9)−C(10), and C(11)−C(12) bonds; a similar trend appears in free bis(*p*-tolylimino)acenaphthene[12] and the Pd complexes with bis(*o*,*o*′-diisopropylphenylimino)-,[12,20] bis(*p*-tolylimino)-,[21] and bis(*p*-anisylimino)acenaphthene.[22] Therefore, analogously to the other BIAN complexes, in **9** the naphthalene backbone shows no significant conjugation with the bisimine moiety. The exocyclic N═C bonds are only slightly longer than those of the free bis(*p*-tolylimino)acenaphthene ligand,[12] suggesting no π back-donation from the metal. Some minor changes in the BIAN moiety of **9** compared to uncoordinated bis(*p*-tolylimino)acenaphthene[12] can be mainly ascribed to coordination to the metal center. Indeed, the C(3)−C(13) bond is shorter in **9** (and in all the cited Pd complexes, 1.49−1.50 Å) compared to the free *p*-tolyl-BIAN ligand (1.535(3) Å); also the torsion angle N(1)−C(3)−C(13)−N(2) (1.9(5)°) is smaller than that in *p*-tolyl-BIAN (−6.5(3)°). This trend, already observed in the Pd-BIAN complexes, reflects the geometric constraints introduced by chelation of the metal. The acenaphthene moiety is planar within experimental error, with a maximum deviation of 0.062(5) Å for C(10), while the donor atoms are 0.186(5) (N(1)) and 0.025(5) (N(2)) Å off the acenaphthene plane. Owing to intramolecular steric crowding, the phenyl groups attached to the imino nitrogen atoms lie significantly off the BIAN plane, with an almost orthogonal disposition for the phenyl bound to N(1) and a tilted conformation for that of N(2), as evidenced by the torsional angles C(3)−N(1)−C(15)−C(16) (−87.7(4)°) and C(13)−N(2)−C(21)−C(22) (−60.8(4)°).

Another interesting feature of compound **9** is the presence of a group derived from the head-to-tail coupling of two 2-tolylisocyanate molecules and giving rise to a five-membered metallacycle through a nitrogen and a carbon donor atom; this moiety lies almost orthogonal to the BIAN ligand (dihedral angle 87.1(1)°). The bond parameters are in agreement with C═O double bonds and sp^2-hybridized N(3), C(27), N(4), and C(28) atoms. The same bond pattern has previously been found in a Pd square-planar complex with a ligand derived from the coupling of two phenylisocyanate molecules.[19]

Conclusions

In this paper we have reported a new catalytic system for the synthesis of allylamines, hetero-Diels−Alder

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adducts, and *N*-arylpyrroles from nitroarenes and unactivated diolefins working under CO pressure. Although selectivities are sometimes low or moderate, it should be considered that alternative synthetic approaches require several steps. In the case of hetero-Diels–Alder adducts, the traditional synthesis requires the isolation of a nitrosoarene, whose preparation usually affords lower yields than the global reaction reported here and is much more experimentally demanding. The synthesis of allylic amines requires in most cases a prefunctionalized compound. Moreover, even the anilines employed in most syntheses are normally prepared by reduction of the corresponding nitroarenes, so that a further step is avoided. Last but not least, the present synthesis does not produce salt byproducts, a feature that is very important in the light of possible industrial applications.

Experimental Section

General Procedure. Unless otherwise specified, all reactions and manipulations were performed either in an autoclave or under a N_2 atmosphere using standard Schlenk apparatus, cannula techniques, and magnetic stirring. Solvents were dried and distilled by standard procedures and stored under dinitrogen. Isoprene was purified by distillation over sodium and stored under dinitrogen before use. Nitrobenzene was purified by shaking with 10% H_2SO_4, washing with water, and drying with Na_2SO_4, followed by distillation under dinitrogen and storage under an inert atmosphere. The Ar-BIAN ligands were synthesized as previously reported.[7] $Ru_3(CO)_{12}$[23] was synthesized as reported in the literature. All other reagents were commercial products and were used as received. Gas chromatographic analyses were performed on a Dani 8610 capillary gas chromatograph equipped with a PS 255 column and coupled to a Perkin-Elmer LCI-100 integrator. Ri values (Ri = response factor, relative to either naphthalene or hexamethylbenzene as an internal standard) were determined by the use of solutions of known concentrations of the compounds. GC–MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph, equipped with a 5971A mass selective detector. NMR spectra were recorded on a Brucker AC 300 FT (300 MHz) at room temperature. When using ^1H NMR to quantify the outcome of catalytic reactions, 2,4-dinitrotoluene was added as an internal standard and a delay of 10 s was applied to ensure complete relaxation of the signals. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

Catalytic Reactions. Catalytic reactions were performed as previously described.[7] Reagents amounts are given in the tables. Those reactions that were repeated showed nitroarene conversion and selectivities to be reproducible within ±1% and ±2% respectively.

Identification of the Organic Products of Catalysis. The byproduct anilines are all commercial products and were identified by comparison of their CG and CG–MS spectra with those of authentic samples. Compounds **1c**,[24] **2b**,[4a] **2c**,[25] **2d**,[26] **2e**,[11] **3b**,[27,28] **3c**,[27,28] **3d**,[27,28] **3e**,[27,28] and **7**[17] are known compounds and were identified by their mass spectra and by comparison of their spectroscopic data with those reported in the literature. In the following, the ^1H NMR spectrum is anyway reported for some of these compounds when these data were not available in the literature or the present spectrum is of significantly better quality than the published one. All compounds were isolated from the reaction mixtures by column chromatography on either silica or neutral alumina (eluant CH_2Cl_2–hexane). The allylic amines are all oils. After the chromatographic separation, no impurity could be detected in the GC and ^1H NMR spectra of the allylamines. Thus the purified compounds are evaluated to be at least 98% pure. The molecular mass peak was always detected in the mass spectra of all allylic amines and pyrroles, but not in the spectra of the hetero-Diels-Alder adducts. For these last compounds, the highest mass peak observable is always the one corresponding to loss of water; that is, conversion to the pyrrole is quantitative in the mass spectrometer.

1a: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.60 (s br, exch. D_2O,1 H, NH), 1.98 (s, 3 H, CH_3), 3.94 (s, 2 H, CH_2), 5.09 (s, 2 H, olefinic protons), 5.22 (s, 1 H, olefinic proton), 5.27 (s, 1 H, olefinic proton), 6.44 (dd, 1 H, $J_{ortho} = 8.7$, $J_{meta} = 2.7$ Hz, Ar), 6.67 (d, 1 H, $J_{meta} = 2.7$ Hz, Ar), 7.19 (d, 1 H, $J_{ortho} = 8.7$ Hz, Ar).

1b: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.96 (s, 3 H, CH_3), 3.93 (s, 2 H, $ArNHCH_2R$), 5.05 (s, 1 H, olefinic proton), 5.10 (s, 1 H, olefinic proton), 5.21 (s, 1 H, olefinic proton), 5.24 (s, 1 H, olefinic proton), 6.48 (d, 2 H, $J = 8.5$ Hz, Ar), 7.06 (d, 2 H, $J = 9.0$ Hz, Ar).

1c: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.96 (s, 3 H, CH_3); 3.96 (s, 2 H, $ArNHCH_2R$); 4.70 (s br, exch. D_2O, 1 H, NH); 5.05 (s, 1 H, olefinic proton); 5.13 (s, 1 H, olefinic proton); 5.24 (s, 2 H, CH_2); 6.58–6.73 (m, 2 H, Ar); 7.12–7.26 (m, 3 H, Ar); ^{13}C NMR ($CDCl_3$) δ, ppm 21.86 (CH_3); 47.45 (CH_2); 113.47 (CH Ar); 113.62 (CH_2); 114.34 (CH_2); 118.09 (CH Ar); 129.86 (CH Ar); 142.12 (C Ar); 142.52 (C); 144.61 (C).

1d: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.6 (s br, exch. D_2O, 1 H, NH), 1.98 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 3.96 (s, 2 H, CH_2), 5.07 (s, 1 H, olefinic proton), 5.14 (s, 1 H, olefinic proton), 5.26 (s, 2 H, olefinic protons), 6.55 (d, 2 H, $J = 8.4$ Hz, Ar), 7.00 (d, 2 H, $J = 8.2$ Hz, Ar).

1e: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.51 (s br, exch. D_2O, 1 H, NH), 1.98 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 3.92 (s, 2 H, CH_2), 5.07 (s, 1 H, CH_2), 5.15 (s, 1 H, CH_2), 5.26 (s, 2 H, CH_2), 6.40–7.00 (4 H, AA′XX′ pattern, aromatic protons); high-resolution mass 203.1316; calcd for $C_{13}H_{17}NO$ 203.1310.

2a: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.66 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 3.65 (s, 2 H, CH_2-N), 4.32 (s, 2 H, CH_2-O), 6.93 (dd, 1 H, $J_{ortho} = 8.8$, $J_{meta} = 2.6$ Hz, Ar), 7.24 (d, 1 H, $J = 2.6$ Hz, Ar), 7.34 (d, 1 H, $J = 8.8$ Hz, Ar). Anal. Calcd for $C_{12}H_{13}Cl_2NO$: C, 55.8; H, 5.0; N, 5.4. Found: C, 55.4; H, 5.1; N, 5.1.

2c: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.65 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 3.67 (s, 2 H, CH_2), 4.34 (s, 2 H, CH_2), 6.89–7.43 (m, 5 H, Ar).

2d: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 1.66 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 3.65 (s, 2 H, CH_2-N), 4.34 (s, 2 H, CH_2-O), 7.06 (d, 2 H, $J = 8.6$ Hz, Ar), 7.13 (d, 2 H, $J = 8.4$ Hz, Ar).

3a: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 2.07 (s, 6 H, CH_3), 6.8 (s, 2 H, pyrrole protons), 7.16 (dd, 1 H, $J_{ortho} = 8.6$, $J_{meta} = 2.2$ Hz, Ar), 7.42 (d, 1 H, $J = 2.2$ Hz, Ar), 7.44 (d, 1 H, $J = 8.6$ Hz, Ar). Anal. Calcd for $C_{12}H_{11}Cl_2N$: C, 60.0; H, 4.6; N, 5.8. Found: C, 59.7; H, 4.2; N, 6.0.

3b: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 2.10 (s, 6 H, CH_3), 6.80 (s, 2 H, pyrrole protons), 7.22 (d, 2 H, $J = 8.9$ Hz, Ar), 7.34 (d, 2 H, $J = 8.8$ Hz, Ar).

3c: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 2.08 (s, 6 H, CH_3); 6.85 (s, 2 H, CH); 7.26–7.38 (m, 5 H, Ar).

3d: ^1H NMR ($CDCl_3$, 298 K) δ, ppm 2.09 (s, 6 H, CH_3), 2.36 (s, 3 H, CH_3), 6.94 (s, 2 H, pyrrole protons), 7.19 (d, 2 H, $J = 8.8$ Hz, Ar), 7.24 (d, 2 H, $J = 8.8$ Hz, Ar).

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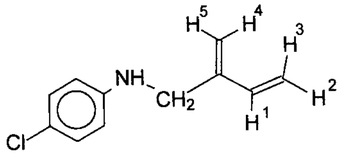
3e: ^{1}H NMR ($CDCl_3$, 298 K) δ, ppm 2.09 (s, 6 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.75 (s, 2 H, pyrrole protons), 6.90−7.30 (4 H, AA′XX′ pattern, aromatic protons).

6



6: ^{1}H NMR ($CDCl_3$, 298 K) δ, ppm 3.93 (s, 2 H, ArNHC*H_2*R), 5.18 (d, 1 H, $J = 10.5$ Hz, H_3), 5.19 (s, 1 H, H_4 or H_5), 5.25 (s, 1 H, H_4 or H_5), 5.32 (d, 1 H, $J = 17.8$ Hz, H_2), 6.47 (dd, 1 H, $J_{cis} = 17.8$, $J_{trans} = 10.5$ Hz, H_1), 6.54 (d, 2 H, $J = 8.8$ Hz, Ar), 7.14 (d, 2 H, $J = 8.8$ Hz, Ar).

7a: ^{1}H NMR ($CDCl_3$, 298 K) δ, ppm 1.79 (s, 3 H, CH_3), 3.62 (s, 2 H, −C*H_2*N−), 4.43 (s, 2 H, −C*H_2*O−), 5.61 (s, 1 H, olefinic proton), 6.98 (d, 2 H, $J = 8.4$ Hz, Ar), 7.17 (d, 2 H, $J = 8.5$ Hz, Ar).

8: ^{1}H NMR ($CDCl_3$, 298 K) δ, ppm 2.18 (s, 3 H, CH_3), 6.20 (ps, 1 H, pyrrole proton), 6.84 (ps, 1 H, pyrrole proton), 6.96 (pt, 1 H, $J = 2.5$ Hz, pyrrole proton), 7.29 (d, 2 H, $J = 8.8$ Hz, Ar), 7.38 (d, 2 H, $J = 8.9$ Hz, Ar). Anal. Calcd for $C_{11}H_{10}ClN$: C, 68.9; H, 5.3; N, 7.3. Found: C, 69.2; H, 5.6; N, 6.9.

Synthesis of Ru[N(*o*-$CH_3C_6H_4$)C(O)N(*o*-$CH_3C_6H_4$)C(O)]-$(CO)_2$(Ph-BIAN) (9). To a glass liner were added $Ru_3(CO)_{12}$ (79.1 mg, 0.124 mmol), *o*-nitrotoluene (172.5 mg 1.258 mmol), and Ph-BIAN (164.5 mg, 0.495 mmol). The liner was placed inside a Schlenk tube with a wide mouth under dinitrogen and was frozen at −78 °C with dry ice, evacuated, and filled with dinitrogen, after which hexane (10 mL) was added. After the solvent was also frozen, the liner was closed with a screw cap having a glass wool-filled open mouth, which allows for gaseous reagent exchange and rapidly transferred to a 200 mL stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO (40 bar) was then charged at room temperature and the autoclave heated at 160 °C for 20 h. At the end of the reaction the liner (containing a red solid and a red solution) was quickly transferred to the Schlenk tube under dinitrogen. The precipitate was collected by filtration and washed with toluene (3 × 10 mL). Yield: 132 mg (46.9%). IR (CH_2Cl_2): 2045 vs, 1982 s, 1650 m, 1603 m, 1494 m, 1457 w, 1451 w, 1365 m, cm^{-1}. Anal. Calcd for $RuC_{42}H_{30}N_4O_4$: C, 66.75; H, 4.00, N, 7.41. Found: C, 64.73; H, 4.41; N, 7.80.

Reaction of 3,4-Dichloronitrobenzene with 2,3-Dimethylbutadiene Catalyzed by Ru[N(*o*-$CH_3C_6H_4$)C(O)N-(*o*-$CH_3C_6H_4$)C(O)]$(CO)_2$(Ph-BIAN). The reaction was performed as the other catalytic reactions, employing **9** (0.090 mmol) instead of $Ru_3(CO)_{12}$ and with a mol ratio **9**/Ph-BIAN/3,4-dichloronitrobenzene = 1:0.33:16.7, at 200 °C, 40 bar CO, in 2,3-dimethylbutadiene (1 mL) + hexane (9 mL) for 6 h. 3,4-Dichloronitrobenzene conversion = 51.4%, pyrrole (**3a**) selectivity = 55.1%, allylic amine (**1a**) selectivity = 8.9%.

X-ray Structure Determination of Ru[N(*o*-$CH_3C_6H_4$)C-(O)N(*o*-$CH_3C_6H_4$)C(O)]$(CO)_2$(Ph-BIAN) (9). A crystal sample of 0.200 × 0.080 × 0.080 mm was mounted on a glass fiber in air at room temperature on a Siemens SMART CCD area-detector diffractometer. Crystal data are reported in Table 6. Graphite-monochromatized Mo Kα radiation (λ 0.71073 Å) was used with the generator working at 45 kV and 40 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on reflections measured in three different sets of 15 frames each, in the range 0° < θ < 23°. The intensity data were collected using the ω-scan technique within the limits 1.77° < θ < 26.07° of a full sphere (1800 frames). Frame width was set at 0.3°, and the detector exposition for each frame was 60 s with the sample−detector distance fixed at 4 cm. The first 60 frames were recollected at the end of the data collection to monitor crystal decay, which was not observed; thus no time-decay correction was needed. The collected frames were processed by software SAINT, and an absorption correction was applied with SADABS[29] on the 34 110 ($R_\sigma = 0.0756$) collected reflections (7086 of which were unique, $R_{int} = 0.0781$). The structure was solved by direct methods (SIR97[30]) and refined with full-matrix least squares on F_o^2 using SHELXL97;[31] anisotropic displacement parameters were assigned to all non-hydrogen atoms. Phenyls were refined as rigid groups with hydrogens riding on their parent carbon atoms. The final conventional agreement indices R_1 and wR_2 are reported in Table 6.

Table 6. Crystal Data and Structure Refinement Parameters for Ru[N(*o*-$CH_3C_6H_4$)C(O)N(*o*-$CH_3C_6H_4$)C(O)]-$(CO)_2$(Ph-BIAN) (9)

chemical formula	$C_{42}H_{30}N_4O_4Ru$
fw	755.77
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	12.168(1)
b, Å	21.878(2)
c, Å	14.682(1)
β, deg	112.96(2)
V, Å^3	3598.9(5)
Z	4
F(000)	1544
D_{calc}, g cm^{-3}	1.395
abs coeff, mm^{-1}	0.483
min rel transm	0.87
T, K	293(2)
scan method	ω
frame width, deg	0.3
time per frame, s	60
no. of frames	1800
index ranges	$-15 \le h \le 14$, $-26 \le k \le 26$, $-18 \le l \le 18$
no. of reflns (total/indep)	34 110/7086
R_{int}, R_σ[a]	0.0781, 0.0756
no. of data/params	7086/412
goodness-of-fit[b] on F_o^2	0.931
R indices [$F_o > 4\sigma(F_o)$]	R1[c] 0.0484, wR2[d] 0.1008
R indices (all data)	R1[c] 0.1206, wR2[d] 0.1214
max diff peak/hole, e Å^{-3}	0.486/−0.350

[a] $R_{int} = \sum|F^2_o - F^2_{mean}|/\sum F^2_o$; $R_\sigma = \sum[\sigma(F^2_o)]/\sum F^2_o$. [b] goof = $[\sum w(F^2_o - F^2_c)^2/(n - p)]^{1/2}$ where n is the number of reflections and p is the number of refined parameters. [c] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [d] wR2 = $[\sum(F^2_o - F^2_c)^2/\sum wF^4_o]^{1/2}$. Weighting scheme: $w = 1/[\sigma^2(F^2_o) + (0.0580P)^2]$ where $P = (F^2_o + 2F^2_c)/3$.

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Supporting Information Available: Full list of atomic coordinates and bond parameters for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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