Allylic Amination of Unactivated Olefins by Nitroarenes, Catalyzed by Ruthenium Complexes. A Reaction Involving an Intermolecular C−H Functionalization

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A reaction is reported, resulting in the allylic amination of an unactivated olefin, cyclohexene, by a nitroarene, catalyzed by $Ru_3(CO)_{12}$/Ar-BIAN (Ar-BIAN = bis(arylimino)-acenaphthene), under CO pressure. The reaction involves an intermolecular catalytic C−H functionalization by a transition metal complex. Best results (selectivity up to 81.9%, with a substrate/$Ru_3(CO)_{12}$ ratio = 50) are obtained by using nitroarenes bearing electron-withdrawing substituents and Ph-BIAN as a ligand. Other olefins can also be employed in place of cyclohexene. The reaction mechanism has been investigated. The reaction is first order in nitroarene and olefin, which is used as solvent in most cases, but the rate equation also contains an olefin-independent term. A rate acceleration by small amounts of toluene in the solvent mixture is due to a faster formation of $Ru(CO)_3$(Ar-BIAN) from $Ru_3(CO)_{12}$ and Ar-BIAN in its presence. This last complex is in equilibrium with the active species Ru(Ar-BIAN)$(CO)_2$(cyclohexene), and its direct reaction with the nitroarene accounts for the olefin-independent term in the rate law. The reaction of $Ru(CO)_3$(Ar-BIAN) with nitroarenes gives $Ru(CO)_2$(Ar-BIAN)(η^2-ArNO), which has been isolated in one case, but this complex is not an intermediate in the synthesis of allylamines. Coupling between a coordinated nitrosoarene and a coordinated olefin appears to be responsible for the C−N bond formation.

Introduction

Transition metal-mediated intermolecular activation and functionalization of C−H bonds is a topic of high current interest. However, with the partial exception of oxidation reactions, few practical reactions have been developed using this approach, and the large majority of them are only stoichiometric in the metal component or show at best a very limited catalytic efficiency.[1] From another perspective, the functionalization of a simple olefin by an external amine is also a topic that has attracted much interest. However, the direct intermolecular addition of an amine to an unactivated olefin, either metal-mediated or not, has met with only a limited success.[2] Good results have only been obtained by using much more reactive nitrogen compounds, such as PhI=NTs (aziridines are usually obtained in this case).[3] As far as allylic amines are considered as products,[4] most reported synthetic procedures proceed via a palladium or nickel[4,5] allyl complex. However, the synthesis of these intermediates usually requires the availability of a prefunctionalized starting material, such as an allyl acetate. A few methods have been reported in the literature, which afford an allylic amine by a C−H activation reaction.[6−14] Stoichiometric reactions have been performed employing sulfur or selenium

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Table 1. Synthesis of Allylamines 1 from Commercial Cyclohexene and Different Nitroarenes[a]

entry no.	nitroarene	ligand	allylamine select. %[b]	aniline select. %[b]
1[c]	$4\text{-MeOC}_6H_4NO_2$	Tol-BIAN	26.3 (**1e**)	15.1
2	$4\text{-MeC}_6H_4NO_2$	Tol-BIAN	55.0 (**1d**)	27.4
3	$PhNO_2$	Tol-BIAN	58.9 (**1c**)	22.8
4	$4\text{-FC}_6H_4NO_2$	Tol-BIAN	63.8 (**1b**)	26.3
5	$3,4\text{-Cl}_2C_6H_3NO_2$	Tol-BIAN	71.1(**1a**)	20.7
6	$3,4\text{-Cl}_2C_6H_3NO_2$	TMPhen	22.4 (**1a**)	34.4
7	$3,4\text{-Cl}_2C_6H_3NO_2$	Ph-BIAN	77.4 (**1a**)	23.4
8	$3,4\text{-Cl}_2C_6H_3NO_2$	4-MeOC_6H_4-BIAN	61.8 (**1a**)	30.5
9	$3,4\text{-Cl}_2C_6H_3NO_2$	4-ClC_6H_4-BIAN	57.7 (**1a**)	29.1
10[d]	$3,4\text{-Cl}_2C_6H_3NO_2$	Tol-BIAN	74.3 (**1a**)	25.5
11[e]	$3,4\text{-Cl}_2C_6H_3NO_2$	DPPE	26.2 (**1a**)	42.7

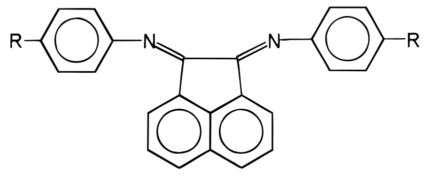
[a] Experimental conditions: $Ru_3(CO)_{12} = 0.01$ mmol, ligand = 0.03 mmol, $ArNO_2 = 0.5$ mmol, $T = 160$ °C, $P_{CO} = 40$ bar, $t = 6$ h, in commercial cyclohexene (10 mL). Conversion = 100%. [b] Calculated with respect to the converted nitroarene; GC analysis. [c] Conversion = 78.3%. [d] $3,4\text{-Cl}_2C_6H_3NO_2 = 1$ mmol, conversion = 86.0%. [e] $Ru(CO)_3(DPPE)$ (0.03 mmol) was used as catalyst, without any added ligand; conversion = 51.6%.

imino compounds (RN═X═NR; X = S, Se)[6] or molybdenum oxaziridines.[7] A few catalytic processes have also been reported employing PhI═NTs,[8] PhNHOH,[9−14] or peroxycarbamates[15] as the nitrogen-containing compound, but the turnover numbers are quite low and the aminating reagents are not readily available.[16] An interesting approach has also more recently been reported,[17] which employs an amine in the presence of an oxidant as the aminating agent, thus avoiding the preliminary synthesis of the hydroxylamine, but the turnover numbers are still low, although selectivities are high in some cases.

In this paper, we report on a new synthetic way to produce allylic amines, employing a simple unactivated olefin, cyclohexene, and an aromatic nitro compound as the aminating reagent, under reducing conditions (CO pressure). Although the method requires the use of a high-pressure apparatus, the reagents are bulk, cheap commercial products that do not need to be purified (although a higher selectivity can be achieved by purifying the olefin), the experimental operations are easy, the selectivity is high (up to 81.9%), and the turnover numbers are higher than those reported for most C−H activation reactions. Only one precedent exists for an analogous reaction also examined in our laboratories,[18] but only trace amounts of allylic amine were obtained in that case, the main products being ureas and anilines.[19,20] A preliminary communication on part of the results reported here has been published.[21]

Results

Synthesis of the Ligands. A synthesis of the Ar-BIAN[22] ligands employed in this study has already been reported.[23,24] The most general procedure requires the reaction of acenaphthenequinone with an aromatic amine in the presence of dry zinc chloride. A zinc chloride complex of the ligand is formed, from which the ligand is liberated by boiling the solid in an aqueous solution of sodium carbonate.

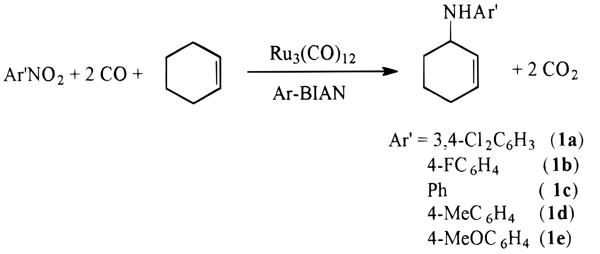


Ar-BIAN

(R = H, Me, OMe, Cl)

We performed the first step of the synthesis as previously reported, but we used a different procedure to free the ligand from the zinc salt. The zinc complex is suspended in CH_2Cl_2 (in which it is moderately soluble), and an aqueous solution of potassium (or sodium) oxalate is added. Simple shaking of the biphasic solution in a separating funnel for a few minutes causes the precipitation of zinc oxalate (which remains as a suspension in the aqueous phase) and complete solubilization of the ligand in the CH_2Cl_2 layer. Usual workup of the organic layer affords the analytically pure ligand in almost quantitative yields (from the zinc complex) and without the need for a recrystallization.

Catalytic Results. The reduction of aromatic nitro compounds, $Ar'NO_2$, by CO catalyzed by $Ru_3(CO)_{12}$ in the presence of Ar-BIAN, in commercial cyclohexene as solvent and at 160 °C and 40 bar, gives the corresponding allylamine derivatives as the main products (eq 1, Table 1):



(1)

Byproducts of the reaction are the anilines corresponding to the nitro compounds. With a substrate/catalyst ratio of 50, only in the case of Ar = 4-MeOC_6H_4 is a complete conversion not achieved (entry 1). More-

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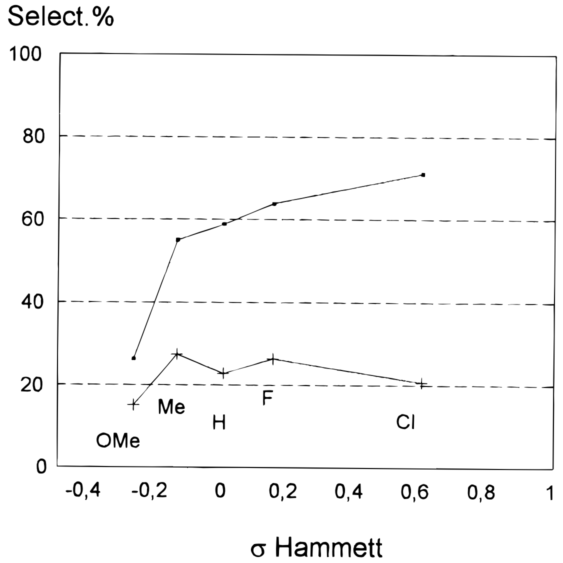

Figure 1. Effect of the substituent on the catalytic intermolecular amination of cyclohexene: (■) selectivity percent in allylamine; (+) selectivity percent in R-aniline. The last point corresponds to $3,4\text{-}Cl_2C_6H_3NO_2$, and the sum of the Hammet σ_p and σ_m values for a chloro substituent was used. The best straight line passing through the last four points in the selectivity in the allylamine series has the equation Select. % = $21.0\sigma + 58.9$, with $R^2 = 0.970$.

over, in this case the reaction shows a poor selectivity. In the other cases, a complete conversion is also accompanied by a much better selectivity. The selectivity increases with an increase in the electron-withdrawing power of the substituent on the nitroarene (Table 1, entries 1–5, Figure 1). A linear relationship exists between the selectivity in allylamine and the Hammet σ constant for all of the nitroarenes employed (the last point in Figure 1 corresponds to $3,4\text{-}Cl_2C_6H_3NO_2$ and the sum of the Hammet σ_p and σ_m values for a chloro substituent was used) except for $4\text{-}MeOC_6H_4NO_2$ (select. % = $21.0\sigma + 58.9$, with $R^2 = 0.970$).

The amount of aniline formed during the reaction is quite insensitive to the nature of the substituents. Its formation may be attributed to the presence of moisture in the solvent and in the CO gas.[25] However, when we employed cyclohexene purified by distillation over sodium under the conditions of entry 5 in Table 1, the selectivity in aniline was slightly changed, although the selectivity in allylic amine increased to 81.9% (with a mass balance of 98.4%). Moreover, we could evidence (by GC–MS) the formation of benzene and cyclohexadiene in the volatile fraction after the end of the reaction The same two products were not present in the starting solvent, and their formation indicates that the substrate itself is responsible for at least part of the aniline formed, but moisture in the undried solvent plays a negligible role. The hydrogen-transfer reduction of nitroarenes by cyclohexene has long been known to be catalyzed by heterogeneous palladium catalysts,[26] but, to the best of our knowledge, this is the first time that this reaction is found to be catalyzed by a homogeneous complex. The higher selectivity obtained with the purified substrate also indicates that, although the commercial olefin is a suitable substrate, it contains some impurities which lower the selectivity, affording unidentified, high-boiling products.

Table 2. Effect of the BIAN/Ru Ratio on the Synthesis of 1a from Purified Cyclohexene and $3,4\text{-}Cl_2C_6H_3NO_2$[a]

run	ligand	ligand/Ru mol ratio	nitroarene conv. %[b]	allylamine select. %[c]	aniline select. %[c]
1	Ph-BIAN	1	30.0	72.0	12.7
2	Ph-BIAN	1.25	33.0	71.0	12.8
3	Ph-BIAN	1.5	31.0	70.9	13.0
4	Ph-BIAN	2	29.8	64.4	12.9
5	Ph-BIAN	3	30.9	65.0	12.2
6	Tol-BIAN	1	32.2	66.6	7.1
7	Tol-BIAN	1.5	37.1	65.2	9.8
8	Tol-BIAN	2	38.5	57.7	6.1
9	Tol-BIAN	3	49.1	40.8	5.0

[a] Experimental conditions: $Ru_3(CO)_{12} = 0.01$ mmol, $ArNO_2 = 1.0$ mmol, $T = 160$ °C, $P_{CO} = 40$ bar, $t = 1.5$ h, in purified cyclohexene (9 mL) + toluene (1 mL). [b] Calculated with respect to the initial nitroarene. [c] Calculated with respect to the converted nitroarene.

We also examined the effect of changing the substituent at the para position on the aryl rings of the ligand. In all cases, the conversion was complete, but the selectivity in allylamine followed the order R = H > Me > OMe > Cl (Table 1, entries 5, 7–9). An influence on the basicity of the ligand is evident, but there is no correlation with the Hammet σ constants. Use of 3,4,7,8-tetramethyl-1,10-phenanthroline (TMPhen) as ligand in place of Ar-BIAN gave much poorer results (entry 6). Phosphines are even less efficient as ligands, even when the preformed complex (see later) $Ru(CO)_3(DPPE)$ (DPPE = 1,2-bis(diphenylphosphino)ethane) was employed (entry 11). Use of other catalytic systems such as Pd(2,4,6-trimethylbenzoate)$_2$/TMPhen[27] or $Rh_4(CO)_{12}$/Bipy[27] also afforded much poorer yields.

At this point we started an optimization study on the reaction conditions. Cyclohexene purified over sodium was used for these and all of the following reactions, and 10% toluene was also added to the solvent mixture as the presence of a small amount of this solvent has been found to increase the rate of the reaction (see later). The use of purified cyclohexene led to much higher reaction rates with respect to the ones obtained in the commercial solvent, and the reaction time had to be reduced to 1.5 h and the catalytic ratio $ArNO_2$/Ru increased to 100 in order to avoid complete conversion of the substrate. We initially examined the effect of changing the ligand/Ru ratio with the two best ligands found in the screening study, Ph-BIAN and Tol-BIAN. As it is evident from the results reported in Table 2, in

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(22) Note that in previous papers we used the name DIAN-R for these ligands. However, since other groups are using the general name Ar-BIAN for this class of ligands and this last terminology is of more general application, we have decided to adhere to this convention in order to avoid the use of different names in the literature for the same compound.

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Table 3. Effect of the Temperature on the Synthesis of 1a from Purified Cyclohexene and 3,4-$Cl_2C_6H_3NO_2$, Catalyzed by $Ru_3(CO)_{12}$ and Ph-BIAN[a]

run	T/°C	nitroarene conv. %[b]	allylamine select. %[c]	aniline select. %[c]
1	155	29.6	55.5	10.5
2	160	33.0	71.0	12.8
3	165	34.4	62.9	8.2
4	170	41.0	59.8	17.6

[a] Experimental conditions: $Ru_3(CO)_{12} = 0.01$ mmol, Ph-BIAN $= 0.0375$ mmol, $ArNO_2 = 1.0$ mmol, $P_{CO} = 40$ bar, $t = 1.5$ h, in purified cyclohexene (9 mL) + toluene (1 mL). [b] Calculated with respect to the initial nitroarene. [c] Calculated with respect to the converted nitroarene.

Table 4. Effect of Pressure on the Synthesis of 1a from Purified Cyclohexene and 3,4-$Cl_2C_6H_3NO_2$, Catalyzed by $Ru_3(CO)_{12}$ and Ph-BIAN[a]

run	P_{CO}/bar	nitroarene conv. %[b]	allylamine select. %[c]	aniline select. %[c]
1	20	31.7	65.2	18.3
2	30	30.3	78.4	16.0
3	40	31.3	78.9	18.0
4	50	34.2	68.8	12.7

[a] Experimental conditions: $Ru_3(CO)_{12} = 0.03$ mmol, Ph-BIAN $= 0.1125$ mmol, $ArNO_2 = 3.0$ mmol, $T = 160$ °C, $t = 1.5$ h, in purified cyclohexene (9 mL) + toluene (1 mL). [b] Calculated with respect to the initial nitroarene. [c] Calculated with respect to the converted nitroarene.

the case of Ph-BIAN, an increase of the ligand/Ru molar ratio from 1 to 3 leads to only very small variations in the nitroarene conversion, with differences close to the experimental error. However, the selectivity in allylamine decreases when the amount of ligand is increased. In the case of Tol-BIAN, an analogous decrease in selectivity is observed in the same series, but this time the conversion regularly increases with an increase in the ligand amount, indicating that even a very small variation in the ligand structure can markedly alter the reaction. The reactions conducted with Ph-BIAN gave better selectivities, but lower conversions with respect to reactions conducted with Tol-BIAN at the same ligand/Ru ratio. The reason for this behavior has been investigated and will be discussed later in this paper.

An increase in the reaction temperature from 150 to 170 °C led to a regular increase in the conversion, but the selectivity was highest at 160 °C (Table 3). A variation in the CO pressure in the range 20−50 bar had a negligible effect on conversion and a moderate effect on selectivity (Table 4). A pressure between 30 and 40 bar gives the best results. Note that the selectivities reported in Tables 2−4 are generally inferior to the highest selectivity (81.9%) obtained in neat cyclohexene and at a 50:1 catalytic ratio for 6 h, but a higher catalytic ratio and a shorter reaction time were necessary to better discriminate the effect of the different variables.

At least part of the decrease in selectivity at higher catalytic ratios is due to the accumulation of the byproduct aniline. Indeed, by adding a molar amount of 3,4-dichloroaniline equal to that of nitroarene to a reaction run under the conditions of entry 5 in Table 1 but for 2 h (using dry cyclohexene), the conversion and selectivity dropped from 95.5% to 64.6% and from 76.8% to 51.0%, respectively.

Another ligand, Ph-BIP (9,10-bis(phenylimino)-9,10-dihydrophenanthrene), analogous to the BIAN ligands mostly employed in this study, was also tested under the conditions of entry 2 in Table 2. A higher conversion (45.2%) was obtained with respect to the use of Ph-BIAN, but with a lower selectivity (48.8% in allylamine and 28.3% in 3,4-dichloroaniline); thus its use was not investigated further.

Table 5. Synthesis of Allylamines Derived from 3,4-$Cl_2C_6H_3NO_2$ and Other Olefins[a]

run	olefin	nitroarene conv. %[b]	allylamine select. %[c]
1	cyclooctene	81.2	57.2 (**1f**)
2	cyclopentene	98.9	37.7 (**1g**)
3	α-methylstyrene	94.5	51.8 (**1j**)

[a] Experimental conditions: $Ru_3(CO)_{12} = 0.01$ mmol, Ph-BIAN $= 0.0375$ mmol, $ArNO_2 = 1.0$ mmol, $T = 160$ °C, $P_{CO} = 40$ bar, $t = 6$ h (unoptimized conditions). The purified olefin was used as solvent (10 mL). [b] Calculated with respect to the initial nitroarene. [c] Calculated with respect to the converted nitroarene.

After all of the catalytic reactions, the only products that could be observed by CG and GC−MS were the allylamine and the aniline. Only during some of the optimization experiments, was a very small peak observed in the gaschromatogram, which showed in the mass spectrum a parent peak at the same mass as the allylamine, but with a different fragmentation pathway. This peak (which typically corresponds to 2−3% that of the allylamine) can be attributed to an isomer of the allylamine, but the available data are not sufficient to indicate if this is the vinyl or the omoallylic isomer and the very small amount of this substance prevented isolation and full characterization. This compound is likely formed by an isomerization of the initially formed allylamine, as the present catalytic system has been shown to be able to isomerize olefins easily (see later). It should be noted that we cannot completely exclude that this byproduct is the aziridine formally derived from cyclohexene and a 3,4-dichlorophenylnitrene, which would show the same parent peak in the mass spectrum as for the allylamine, although we have obtained no evidence for the formation of such products in our reactions. Any other nitroarene-derived byproduct appears to be polymeric and was not investigated. A very small amount of a product showing in the GC−MS spectrum a peak with a mass corresponding to a dimer of cyclohexene was also observed in some cases.

The reaction is not limited to cyclohexene as substrate, and cyclopentene, cyclooctene, and α-methylstyrene also afford moderate to good yields of the desired adduct (Table 5). However, 1-hexene gave only poor yields of a mixture of isomeric adducts, accompanied by isomerization of the unreacted olefin to a mixture of 1-, 2-, and 3-hexene, and allyl alcohol reacted as an alcohol, to afford the carbamate 3,4-$Cl_2C_6H_3NHCOOCH_2CH{=}CH_2$, as it is common in this kind of system.

The rate of the isomerization reaction of the starting olefin is much higher than that of the amination reaction, and this fact prevented us from assessing the regiochemistry of the amination reaction in more detail.

Kinetic Studies. The results above-reported for the $Ru_3(CO)_{12}$/Ar-BIAN catalytic system suggest that the reaction rate depends on the nitroarene concentration. The reaction conducted on 3,4-$Cl_2C_6H_3NO_2$ and cyclohexene under the usual catalytic conditions was also followed by using a high-pressure IR cell. Plotting the

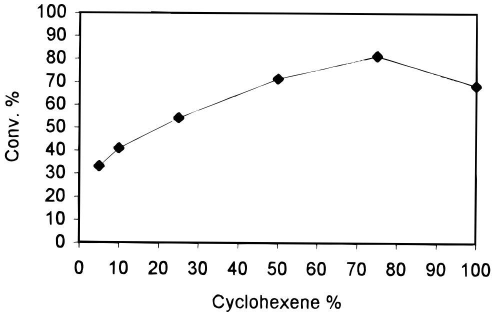

Figure 2. 3,4-$Cl_2C_6H_3NO_2$ conversion percent as a function of the volume percent of cyclohexene in the solvent mixture, the remaining being toluene. Experimental conditions: 3,4-$Cl_2C_6H_3NO_2$ = 1 mmol, $Ru_3(CO)_{12}$ = 0.01 mmol, Tol-BIAN = 0.045 mmol, T = 160 °C, P_{CO} = 40 bar, for 1 h, in cyclohexene/toluene (total volume 10 mL).

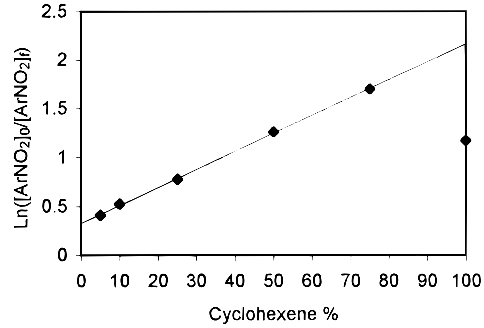

Figure 3. Plot of the function $\ln([ArNO_2]_0/[ArNO_2]_f)$ as a function of the volume percent of cyclohexene in the solvent for the reaction described in Figure 2. $[ArNO_2]_0$ = concentration of 3,4-$Cl_2C_6H_3NO_2$ at the beginning of the reaction; $[ArNO_2]_f$ = concentration of 3,4-$Cl_2C_6H_3NO_2$ at the end of the reaction.

ln(absorbance) for the $\nu_{as\ NO2}$ at 1540 cm^{-1} versus time gave a straight line (R^2 = 0.996), clearly indicating a first-order dependence of the reaction rate on the nitroarene concentration.

The rate was also found to be a function of the olefin concentration. Use of mixtures of cyclohexene and toluene (both purified over sodium) as solvents led to the observation that the reaction rate linearly increases as the olefin concentration is increased from 5% of the total volume to 75%, but then decreases when only the olefin is used as solvent, indicating a positive effect of the presence of a small amount of toluene, which will be discussed in more detail later in this paper. The data collected (see Figures 2 and 3) show that the rate follows the equation $-d[3,4\text{-}Cl_2C_6H_3NO_2]/dt = [3,4\text{-}Cl_2C_6H_3NO_2](k[\text{cyclohexene}] + c)$, with k = 0.186 L h^{-1} mol^{-1}, c = 0.331 L h^{-1}, and R^2 = 0.9994 (at 160 °C and under 40 bar CO). This equation indicates the rate is also first order in olefin, but the nonzero intercept in Figure 3 indicates that there is a contribution from an olefin-independent reaction (see also later).

The selectivity in allylamine is also a function of the olefin concentration, but there is no linear relationship between the two (Figure 4).

Formation of Organometallic Intermediates. To gain more information on the identity of the catalytically active species, we have investigated the reactivity of $Ru_3(CO)_{12}$ with several BIAN ligands. It is known that $Ru_3(CO)_{12}$ reacts in refluxing *n*-hexane with a nonrigid alkyl diazabutadiene derivative, *i*PrN=C(Me)–C(Me)=N*i*Pr (*i*Pr-DAB), to give a mononuclear complex (eq 2):[28]

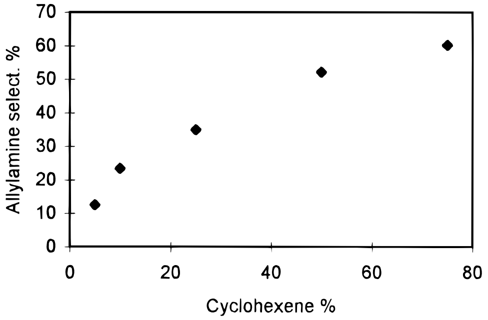

Figure 4. Selectivity in allylamine **1a** as a function of the volume percent of cyclohexene in the solvent for the reactions described in Figure 2.

$$Ru_3(CO)_{12} + 3\ i\text{Pr-DAB} \xrightarrow[N_2]{n\text{-hexane, reflux}} 3\ Ru(CO)_3(i\text{Pr-DAB}) + 3\ CO \quad (2)$$

When an analogous reaction was performed in Decaline or toluene at 110 °C, using 2,6-*i*$Pr_2C_6H_3$-BIAN ligand instead of R-DAB and in a 3:1 molar ratio with respect to $Ru_3(CO)_{12}$, the analogous complex $Ru(CO)_3$(2,6-*i*$Pr_2C_6H_3$-BIAN) (**2a**) could be isolated in analytically pure form and was characterized by spectroscopic means. In particular, the IR spectrum of **2a** (in Decaline) showed three bands in the carbonyl region at 2044 (s), 1978 (m), and 1972 (m) cm^{-1}, to be compared with the ones at 2040 (s) and 1967 (s) reported for $Ru(CO)_3$(*i*Pr-DAB) in *n*-hexane.[28] The splitting of the lower frequency band in the carbonyl region of **2a** is clearly due to the more rigid structure of Ar-BIAN with respect to *i*Pr-DAB. The use of 2,6-*i*$Pr_2C_6H_3$-BIAN as a model ligand is justified by the fact that it could also be employed in catalytic reactions, although both conversion and selectivity were lower than those obtained with Ph-BIAN or Tol-BIAN. In the case of Ph-BIAN and Tol-BIAN, the same kind of complex was clearly formed (**2b** and **2c**, respectively), on the basis of the IR and ^{1}H NMR data, but the complexes could not be isolated in an analytically pure form due to their very high reactivity and solubility. For these last two ligands, the reaction is much faster and is complete in a few minutes in refluxing *n*-hexane or in toluene at 60 °C, but a 6:1 ratio BIAN/$Ru_3(CO)_{12}$ had to be used (analogously to what was reported for the *i*Pr-DAB reaction) in order to avoid formation of polynuclear complexes. Apparently, the larger steric hindrance of 2,6-*i*$Pr_2C_6H_3$-BIAN completely inhibits the dimerization reactions and even the sensitivity to dioxygen of the product is somewhat reduced. Interestingly, we found that the reaction between Ru_3-

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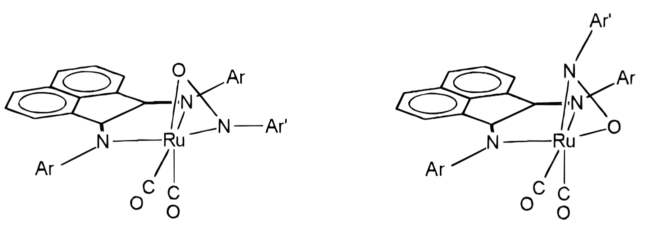
[28] Kraakman, M. J. A.; Vrieze, K.; Kooijman, H.; Spek, A. L. *Organometallics* **1992**, *11*, 3760.

[29] Solutions of **2b** and **2c** are not stable, and upon long standing at room temperature under dinitrogen, a yellow precipitate is formed, showing in the IR spectrum (in toluene) two main bands at 2036 and 1974 (for **2c**) cm^{-1}. In the FAB$^+$ mass spectrum of this material, a peak was observed attributable to a complex with the stoichiometry $Ru_2(CO)_4$(Tol-BIAN)$_2$, but the elemental analysis was not consistent with this attribution and, moreover, was not constant from one preparation to another. Thus this material appears to be a mixture and was not investigated further. Several different di- and trinuclear ruthenium carbonyl complexes containing the *i*Pr-DAB ligand have already been characterized.[30]

Scheme 1



3A **3B**

Ar = 2,6-$iPr_2C_6H_3$
Ar' = 2-CF_3,4-ClC_6H_3

$(CO)_{12}$ and all BIAN ligands is inhibited by just one atmosphere of CO, and even the easy synthesis of **2b** and **2c** is not complete after several hours in refluxing *n*-hexane in its presence. As later discussed in more detail, this fact is relevant to the formation of the catalytically active species under catalytic conditions, where a much higher CO pressure is applied.[29]

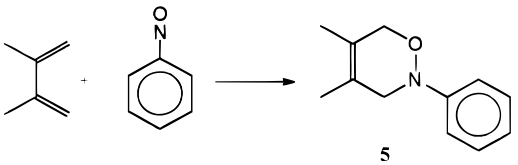
Complexes **2** react instantaneously with nitroarenes at room temperature. The reaction is fast even with a deactivated nitroarene such as 3,4-$(MeO)_2C_6H_3NO_2$, contrary to what has been reported for $Ru(CO)_3$-(DPPE),[31] indicating that the BIAN-containing complexes are much more reactive than the diphosphine-containing one. In the cases of **2b** and **2c**, complete decomposition of the starting material, accompanied by the disappearance of any IR absorption band in the region of the carbonyl ligands, was always observed under any condition. However, in the case of the more hindered **2a**, an isolable complex (**3**) could be obtained when working with 4-Cl,2-$CF_3C_6H_3NO_2$. This last nitroarene has been previously used by Skoog and Gladfelter in a reaction with $Ru(CO)_3$(DPPE) and allowed for the isolation of an otherwise unstable nitrosoarene complex.[31] The formation of a complex **4**, which appears to be analogous to **3** on the basis of the similarity in the IR spectrum, was also observed when **2a** was reacted with 3,4-$Cl_2C_6H_3NO_2$, but this complex decomposed in solution and could not be isolated.

The mass spectrum and elemental analysis of complex **3** indicates it is the nitrosoarene complex $Ru(CO)_2$(2,6-$iPr_2C_6H_3$-BIAN)(η^2-ONC_6H_3-4-Cl,2-CF_3). This complex showed in its IR spectrum two bands at 2012 and 1946 cm^{-1} (in toluene), indicating cis coordination of the two CO groups. In the ^1H NMR spectrum, four signals for the isopropyl C$-$*H* were observed, indicating complete inequivalence of the isopropyl groups. In the ^{19}F NMR of **3**, only one signal was observed for the C*F*$_3$ group of the nitrosoarene, indicating that only one of the two possible isomers, the nitroso oxygen trans to CO or to a BIAN nitrogen, has been formed. Based on the similarity of our compound to the analogous DPPE complex for which the X-ray structure has been reported,[31] we propose structure **3A** for the present complex, although structure **3B** is also consistent with the available data and cannot be completely excluded (Scheme 1).

Complex **3** did not react with cyclohexene at temperatures up to 50 °C. When it was reacted in neat cyclohexene under catalytic conditions (160 °C, 40 bar CO), only the aniline 4-Cl,2-$CF_3C_6H_3NH_2$ was obtained as a product, despite the fact that the corresponding allylamine was clearly observed as the dominant product when a normal catalytic reaction was run employing 4-Cl,2-$CF_3C_6H_3NO_2$ as the aminating agent. This fact is consistent with the data on the selectivity upon varying the olefin concentration, which will be discussed later.

Identification of the Organic Intermediates. Metal-catalyzed nitroarene carbonylation in the presence of alcohols is known to produce carbamates.[32] Anilines have been shown to be intermediates in these reactions in several cases,[33−36] most notably when the reaction was catalyzed by $Ru(CO)_3$(DPPE) or $Ru_3(CO)_{12}$.[33,36] To ascertain if the aniline is only a byproduct or an intermediate of the reaction reported here, one experiment was carried out by using 3,4-$Cl_2C_6H_3NO_2$ as substrate, but also adding unsubstituted aniline to the reaction mixture. Only the adduct containing the substituted aryl ring and no adduct derived from aniline was detected among the products. Thus aniline is clearly not an intermediate in the reaction leading to the allylamine, although the aforementioned lower selectivity when the aniline is also added indicates that it may be an intermediate in the synthesis of one or more of the polymeric byproducts.

Other possible organic intermediates are nitrosoarenes. Allylic amination of olefins by hydroxylamines catalyzed by molybdenum complexes[10] and by iron phthalocyanine complexes[12] has been found to proceed through the formation of free nitrosoarene, which then reacts with the olefin in an "off metal" reaction called "ene reaction"[37,38] to afford a hydroxylamine. This is in turn reduced by the metal complex to the allylic amine. However, in the case of the iron salts-catalyzed reaction, an active role of free nitrosoarenes was excluded.[14] As a test for the involvement of free nitrosoarenes in reactions of this kind, the authors of these works have performed their catalytic reactions in the presence of a diene as the olefin. Indeed dienes react with free nitrosoarenes to yield the hetero Diels−Alder adduct (eq 3)[37,39] instead of the hydroxylamine, and the absence of this product is strong evidence against the formation of the free nitrosoarene.



5 (3)

No allylic amine was formed during reaction 3, even when the nitrosobenzene was added (by means of an high-pressure reservoir) to a solution of the olefin preheated to 160 °C and under 40 bar CO, but in the absence of the metal.

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(30) (a) Mul, W. P.; Elsevier: C. J.; Frühauf, H.-W.; Vrieze, K., Pein, I.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chem.* **1990**, *29*, 2336. (b) Polm, L. H.; Elsevier: C. J.; van Koten, G.; Ernsting, J. M.; Stufkens, D. J.; Vrieze, K.; Andréa, R. R.; Stam, C. H. *Organometallics* **1987**, *6*, 1096.

(31) (a) Skoog, S. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 11049. (b) Skoog, S. J.; Campbell, J. P.; Gladfelter, W. L. *Organometallics* **1994**, *13*, 4137.

(32) Cenini, S.; Ragaini, F. *Catalytic Reductive Carbonylation of Organic Nitro Compounds*; Kluwer Academic Publishers: Dordrecht, 1997; Chapter 3, and references therein.

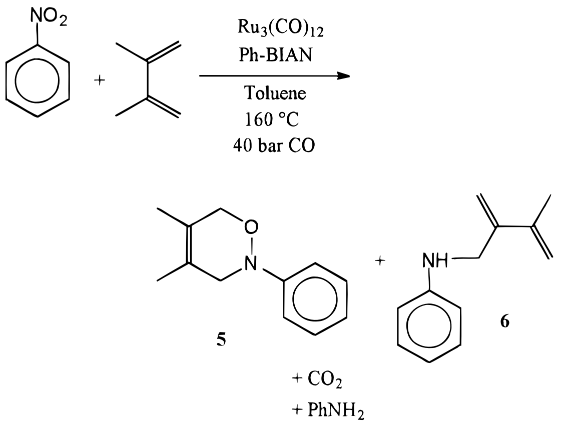
(33) Gargulak, J. D.; Berry, A..J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 8933.

(34) Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1994**, *13*, 1178.

(35) Ragaini, F.; Cenini, S. *J. Mol. Catal. (A)* **1996**, *109*, 1.

(36) Ragaini, F.; Ghitti, A.; Cenini, S. *Submitted.*

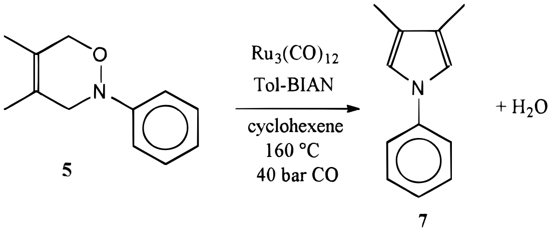
Experiments conducted in other groups generally gave either only the hetero Diels–Alder adduct or only the allylic amine, thus allowing for a clear differentiation. However, in our case, reaction of nitrobenzene with 2,3-dimethylbutadiene under typical catalytic conditions gave a mixture of the hetero Diels–Alder adduct **5** and allylamine **6** in an approximately 3:1 molar ratio (by GC) (eq 4), together with small amounts of aniline.



(4)

The **5**/**6** ratio was insensitive to the olefin amount (0.5, 1, or 2 mL, the complement to 10 mL being toluene), indicating that the competition between the two processes is not influenced by the olefin concentration. On the other hand, the reaction rate increased along the series (nitrobenzene conversion 42, 60, and 65%), analogously to what is observed in the case of cyclohexene (vide supra), indicating that the two processes leading to **5** and **6** share a common rate-determining step. If 3,4-dichloronitrobenzene was used in place of nitrobenzene, the corresponding two products were obtained, although in this case the products were not isolated and characterization is only based on the GC–MS analysis and the analogy with the previous reactions. When this last reaction was repeated in the presence of unsubstituted aniline, only the hetero Diels–Alder adduct derived from the nitroarene was detected, indicating that the presence of a conjugated diolefin does not allow for a reaction of the aniline not available in the other cases. The **5**/**6** ratio was influenced neither by a lower reaction temperature (80 °C) nor by a change in the CO pressure from 20 to 50 bar.

To be sure that **6** does not derive from a following reaction of **5**, the stability of this last product was investigated. Compound **5** is stable under the reaction conditions but in the absence of metal, both in toluene and in cyclohexene. However, in cyclohexene and in the presence of the catalytic system, partial transformation to yield the pyrrole was observed upon prolonging the reaction time, but no allylic amine (derived either from the diene or from cyclohexene) was observed (eq 5):



(5)

The formation of the pyrrole from the hetero Diels–Alder adduct is not completely unprecedented, and the same reaction has been reported to be catalyzed by $[Rh(COD)Cl]_2$ under CO pressure, although use of $Co_2(CO)_8$ afforded a CO inserted product.[40,41] Thus it is clear that **6** must derive from an independent pathway.

Although we have not investigated this reaction in more detail up to now, it is worth noting that by conducting reaction 3 for a prolonged time, good yields of the pyrrole may be obtained directly from the nitroarene and the diolefin, thus representing a new versatile synthesis of *N*-arylpyrroles.

High-Pressure IR Studies. To get more information on the real catalytic system, a series of high-pressure IR spectra were recorded. The cluster $Ru_3(CO)_{12}$ is known to be in equilibrium under CO pressure and in inert solvents with $Ru(CO)_5$, and under conditions similar to ours, the equilibrium is almost completely shifted on the side of the mononuclear complex.[42] In our experiments we found the following.

(a) In the absence of Ar-BIAN, $Ru_3(CO)_{12}$ very slowly converts into $Ru(CO)_5$ up to an equilibrium position shifted on the side of this last product (at 160 °C and 45–50 bar CO) both in *n*-hexane and cyclohexene. Even in this second case, no bands in the carbonyl region were observed apart from those attributable to the two aforementioned compounds. In particular no bands were observed that may be attributable to $Ru(CO)_4$(cyclohexene). This last compound has never been reported in the literature, but the analogous complexes with other olefins[43] are known and their IR bands should fall close to the ones expected for $Ru(CO)_4$(cyclohexene), in a region that is at least in part free from the absorptions of both $Ru_3(CO)_{12}$ and $Ru(CO)_5$.[44]

(b) In *n*-hexane, $Ru_3(CO)_{12}$ reacts with Ar-BIAN to give, as the only primary product, $Ru(CO)_3$(Ar-BIAN). This last complex, in turn, partly transforms on a longer time scale into $Ru(CO)_5$, until an equilibrium is reached. It is interesting to note that the equilibrium between $Ru(CO)_3$(Ar-BIAN) and $Ru(CO)_5$ is more shifted on the side of the Ar-BIAN complex for Ar = Ph than for Ar = Tol under all conditions. In particular, at a 2:1 Ar-BIAN/Ru ratio (at 160 °C and 45 bar CO), the equilibrium is almost completely shifted on the side of the Ar-BIAN complex in the case Ar = Ph, but appreciable amounts of $Ru(CO)_5$ are still present for Ar = Tol (Figure 5).

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[37] Zuman, P.; Shah, B. *Chem. Rev.* **1994**, *94*, 1621.

[38] (a) Knight, G. T. *J. Chem. Soc., Chem. Commun.* **1970**, 1016. (b) Banks, R. E.; Haszeldine, R. N.; Miller, P. J. *Tetrahedron Lett.* **1970**, 4417. (c) D. Mulvey, W. A. Waters *J. Chem. Soc., Perkin. Trans. 2* **1978**, 1959.

[39] Boger, D. L.; Weinreb, S. N. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: New York, 1987.

[40] (a) Okuro, K.; Dang, T. D.; Khumtaveeporn, K.; Alper, H. *Tetrahedron Lett.* **1996**, *37*, 2713. (b) The formation of the pyrrole is probably a more general phenomenon at even higher temperature, even in the absence of the metal, as some **7** is always formed during the gas chromatographic analysis of **5** and, in the EI mass spectrum of **5**, the peak at highest mass observable corresponds to **7**.

[41] (a) Analogous reactions have been reported even for more complex systems.[41b] (b) Streith, J.; Defoin, A. *Synlett* **1996**, 189.

[42] (a) Bor, G. *Pure Appl. Chem.* **1986**, *58*, 543. (b) Koelliker, R.; Bor, G. *J. Organomet. Chem.* **1991**, *417*, 439.

[43] (a) Leadbeater, N. E. *J. Chem. Soc., Dalton Trans.* **1995**, 2923. (b) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* **1981**, *103*, 4069.

[44] In our first communication on this subject,[21] we said that a strong band at 1992 cm^{-1} was observed in cyclohexene. However, this band was later shown to be the result of the use of commercial cyclohexene in that experiment. When purified cyclohexene was employed (as in all spectra reported in this paper) this band was no longer observed.

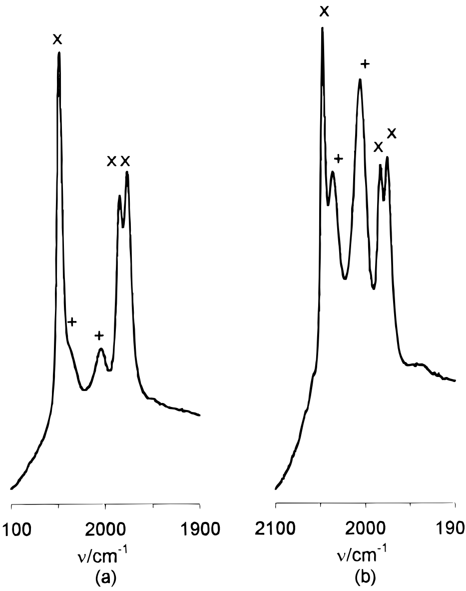

Figure 5. High-pressure IR spectra of solutions of $Ru_3(CO)_{12}$ and Ar-BIAN in *n*-hexane (molar ratio Ar-BIAN/Ru = 2) after 1 h 30 min at 160 °C and P_{CO} = 45 bar. (a) Ar = Ph, (b) Ar = Tol, × = $Ru(CO)_3$(Ar-BIAN), + = $Ru(CO)_5$.

(c) In cyclohexene and in the presence of Ar-BIAN, the same species are observed as in *n*-hexane. The equilibrium is still almost completely shifted on the side of $Ru(CO)_3$(Ar-BIAN) in the case of Ar = Ph (under the same conditions of the spectra in Figure 5, except for the solvent), but it is now markedly shifted on the side of $Ru(CO)_5$ for Ar = Tol.

(d) In an attempt to observe a complex containing a coordinated olefin, we examined a reaction between $Ru_3(CO)_{12}$ and Ph-BIAN in the presence of 2,3-dimethylbutadiene (and *n*-hexane as a cosolvent), in the hope that the higher coordinating power of the diolefin allowed for the observation of a product of substitution of CO. The reaction initially proceeded in the usual way, generating $Ru(CO)_3$(Ph-BIAN). Only at 160 °C is a following reactions observed, which is not complete even after several hours at this temperature. However, spectra subtraction clearly evidenced the disappearance of the bands of $Ru(CO)_3$(Ph-BIAN) and the appearance of three new bands, which grow at the same time at 2062, 1999, and 1987 cm^{-1}. These bands are inconsistent with the formation of a complex in which one or two COs have been substituted by the olefin, but are identical with those reported in the literature for $Ru(CO)_3(\eta^4$-2,3-dimethylbutadiene).[45] Thus it is clear that, on a longer time scale, Ar-BIAN can be substituted by a diolefin.

(e) During a typical catalytic reaction, conducted with a 2:1 Ph-BIAN/Ru ratio, the species largely predominant at 160 °C is $Ru(CO)_3$(Ph-BIAN) (Figure 6).

(f) The reaction between $Ru_3(CO)_{12}$ and Ar-BIAN to yield $Ru(CO)_3$(Ar-BIAN) is not fast under CO pressure both in *n*-hexane and in cyclohexene even at high temperature, in accord with the inhibiting effect of just one atmosphere of CO noted previously. However, the addition of toluene (10 vol %) to cyclohexene notably increases its rate, as evidenced by the comparison of spectra run after the same time in parallel reactions (Figure 7).

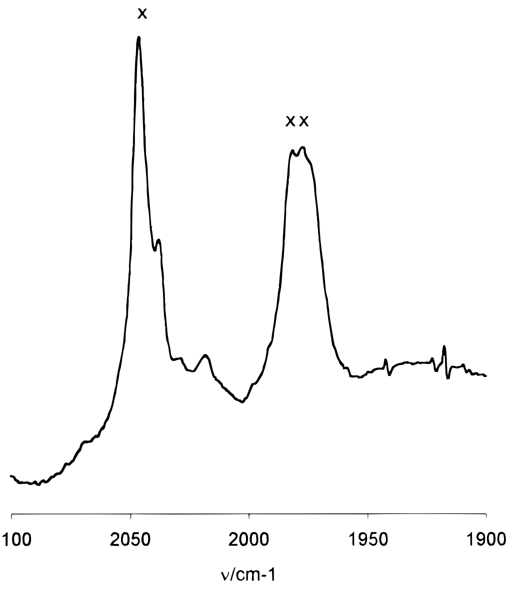

Figure 6. High-pressure IR spectrum of the solution during a catalytic reaction in cyclohexene 20 min after reaching the final temperature. Molar ratio Ph-BIAN/Ru = 2, at 160 °C and P_{CO} = 45 bar. × = $Ru(CO)_3$(Ar-BIAN).

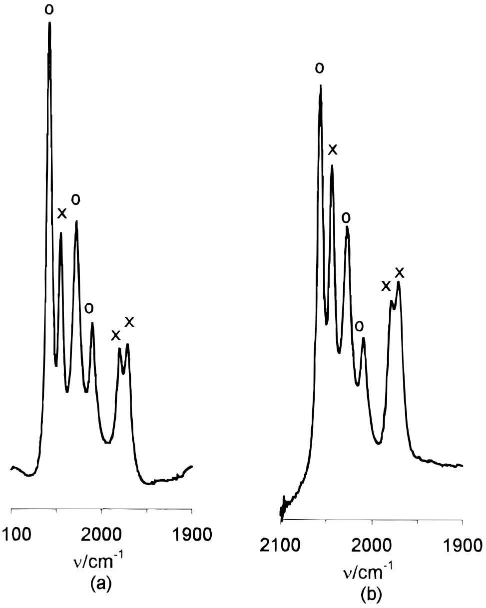

Figure 7. High-pressure IR spectra of solutions of $Ru_3(CO)_{12}$ and Tol-BIAN (molar ratio Tol-BIAN/Ru = 2) after 5 min at 120 °C and P_{CO} = 43 bar: (a) in neat cyclohexene, (b) in cyclohexene + toluene 9:1, × = $Ru(CO)_3$(Ar-BIAN), ○ = $Ru_3(CO)_{12}$.

The effect is only a kinetic and not a thermodynamic one. Indeed, once equilibrium is reached, the amount of $Ru(CO)_3$(Tol-BIAN) with respect to $Ru(CO)_5$ and $Ru_3(CO)_{12}$ is essentially the same both in neat cyclohexene and in cyclohexene/toluene.

Discussion

In this paper we have reported a new reaction affording allylic amines from nitroarenes and unacti-

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

vated olefins. Although the range of substrates screened is still limited, the very large number of nitroarenes and olefins commercially available at a low price renders this methodology appealing. The optimization study, which was performed by using cyclohexene and 3,4-dichloronitrobenzene as substrates, has given the somewhat unexpected result that the conditions we had initially selected based on our experience in other carbonylation reactions of nitroarenes were indeed very close to the optimal ones. Despite the fact that this result did not allow us to further increase the selectivity of the reaction with respect to the early results, a large amount of data has been collected that allow us now to trace a clearer picture of the reaction mechanism. As the synthetic aspects of the reaction do not need to be analyzed in any more detail, the present discussion will mostly focus on the mechanistic aspects of the reaction.

The cluster $Ru_3(CO)_{12}$ was already known to react with diazabutadiene to afford mononuclear complexes (eq 2), and all Ar-BIAN ligands behave in this same way. No cluster species containing the Ar-BIAN ligand was obtained or observed by high-pressure IR under conditions similar to the ones used in catalysis. The use of high-pressure IR spectroscopy also allowed us to understand the different effect of changing the ligand concentration for Ph-BIAN and Tol-BIAN. As it is evident from the results reported in Table 2, in the case of Ph-BIAN, an increase in the ligand/Ru molar ratio from 1 to 3 leads to only very small variations in the nitroarene conversion, whereas in the case of Tol-BIAN, the conversion regularly increased with an increase in the ligand amount. What we found is that under CO pressure an equilibrium is set between $Ru(CO)_3$(Ar-BIAN) and $Ru(CO)_5$ (eq 6), and this equilibrium is more shifted on the side of the Ar-BIAN complex for Ar = Ph than for Ar = Tol.

$$Ru(CO)_3(\text{Ph-BIAN}) + 2\ CO \rightleftharpoons Ru(CO)_5 + \text{Ar-BIAN} \qquad (6)$$

Thus it appears that a 1.25:1 ratio Ph-BIAN/Ru (under the concentration, temperature, and pressure conditions employed) is sufficient to keep almost all the ruthenium in the form of $Ru(CO)_3$(Ph-BIAN), and any further increase in the ligand amount is not influential with respect to the equilibrium in eq 6. On the other hand, a complete shift to the left of the same equilibrium is not reached for Ar = Tol even for a 3:1 Tol-BIAN/Ru ratio under the same conditions, thus explaining the continuous rate increase with the increase in Tol-BIAN amount. The weaker coordinating ability of Tol-BIAN with respect to Ph-BIAN toward $Ru(CO)_3$ is not completely unexpected, given the thermodynamic preference of this fragment for CO and its low oxidation state. Indeed the Tol-BIAN ligand is more electron-donating than Ph-BIAN, as also evidenced by the position of the IR bands in the $Ru(CO)_3$(Ar-BIAN) complexes and by the position of the NMR signals and the oxidation potentials of the complexes $PdCl_2$(Ar-BIAN).[46] Very recently, it was shown[47] that arylphosphines bearing electron-withdrawing groups on the aryl rings bind to a palladium(0) complex more strongly than those bearing electron-releasing groups.

It should be noted that this effect of the ligand concentrations on the rate of the catalytic reactions clearly indicates that the active species must contain a coordinated Ar-BIAN, and the effect of the ligand is not just to accelerate the breaking of the cluster to ultimately afford $Ru(CO)_5$.[48] Why an increase in the ligand amount lowers selectivity is not clear at this stage. However, it can be excluded that this effect is due to the formation of more substituted species such as Ru(CO)$(\text{Ar-BIAN})_2$, as their formation should considerably alter the kinetics of the reaction, and moreover no spectroscopic evidence for the formation of any such species has been obtained under any conditions.

The formation of $Ru(CO)_3$(Ar-BIAN) as the only primary product of the reaction between $Ru_3(CO)_{12}$ and Ar-BIAN and its only subsequent equilibration with $Ru(CO)_5$ is worth more comment. Chelating ligands have long been known to induce fragmentation of $Ru_3(CO)_{12}$ to mononuclear species containing the ligand,[49] but, to the best of our knowledge, this is the first time that this process is shown to be kinetically controlled and not thermodynamically driven. In other words, at least in this case, formation of the substituted mononuclear compound does not proceed because this product is more stable than both $Ru_3(CO)_{12}$ and $Ru(CO)_5$, but simply because the reaction of a basic ligand with the cluster is faster than that of CO. Once formed, the $Ru(CO)_3$(L−L) complex may even be unstable with respect to the conversion to $Ru(CO)_5$. This has implications even for other catalytic carbonylation systems in which a complex of the type $Ru(CO)_3$(L−L) is the active species. Indeed, there are surely experimental conditions under which the catalytic system will deactivate with time not because of the formation of aggregated species, as it is most often proposed in these cases, but because of the conversion of the active species into $Ru(CO)_5$. Retrospectively, this was surely the case in some of the reactions reported in this paper. A reinvestigation of several ruthenium-based carbonylation catalytic systems with an eye to this problem would probably lead to an improvement of the catalysts' performances.

The first-order dependence of the reaction rate upon the nitroarene concentration indicates that the initial activation of the nitroarene is the rate-determining step of the catalytic cycle, and the fact that the only substrate for which a complete conversion was not achieved is the one with a para-methoxy group, that is the one with the most electron-releasing group among those tested, suggests that, analogously to all other investigated Ru,[31,50] Rh,[34] Fe,[51] and Ni[52] systems, this activation is an electron transfer from the complex to the nitroarene.

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[46] van Asselt, R.; Elsevier: C. J.; C. J. Amatore, C. J.; Jutand, A. *Organometallics* **1997**, *16*, 317.

[47] Amatore, C.; Jutand, A.; Meyer, G. *Inorg. Chim. Acta* **1998**, *273*, 76.

[48] We have recently shown[36] that in the $Ru_3(CO)_{12}$/$[Et_4N][Cl]$ catalytic system for the carbonylation of nitroarenes to carbamates one role of chloride is just to accelerate the conversion of $Ru_3(CO)_{12}$ into the catalytically active $Ru(CO)_5$ and the halide does not bind to any intermediate in the effective catalytic cycle.

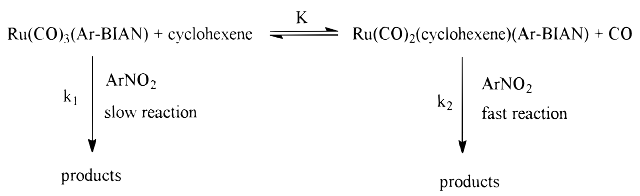
[49] Sanchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 399.

[50] (a) Sherlock, S. J.; Boyd, D. C.; Moasser, B.; Gladfelter, W. L. *Inorg. Chem*. **1991**, *30*, 3626. (b) Kunin, A. G.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2739.

[51] (a) Ragaini, F.; Song, J.-S.; Ramage, D. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 387. (b) Belousov, Yu. A.; Kolosova, T. A. *Polyhedron* **1987**, *6*, 1959.

[52] Berman, R. S.; Kochi, J. K. *Inorg. Chem*. **1980**, *19*, 248.

Scheme 2



The electron-transfer nature of the rate-determining step explains why a higher conversion is generally observed when Tol-BIAN is used in place of Ph-BIAN, despite the fact that more “active species” should be present at the equilibrium in the latter case.

The reaction rate has been found to be first order in olefin concentration, but with an olefin-independent term. As it is very unlikely that the rate-determining step is a single act involving a ruthenium complex, the olefin, and the nitroarene and since the interaction of the complex with the nitroarene is surely irreversible, the best explanation for the observed rate is that a fast preequilibrium exists between $Ru(CO)_3(Ar\text{-}BIAN)$ and an olefin-containing complex and the latter reacts with the nitroarene at a faster rate (Scheme 2).

The direct reaction of $Ru(CO)_3(Ar\text{-}BIAN)$ with the nitroarene would account for the olefin-independent term in the rate. As cyclohexene should be a poorer electron acceptor with respect to CO, the olefin complex should be more reactive toward nitroarenes, and the relatively large difference in reactivity shown by the Tol-BIAN and Ph-BIAN complexes supports the idea that even small differences in the donating/accepting power of the ligands can profoundly alter the rate of this reaction.

A process such as the one depicted in Scheme 2 should in general follow a rate equation of the type

$$-\mathrm{d}[\mathrm{ArNO_2}]/\mathrm{d}t = [\mathrm{ArNO_2}](k_1[\mathrm{Ru(CO)_3(Ar\text{-}BIAN)}] + k_2[\mathrm{Ru(CO)_2(olefin)(Ar\text{-}BIAN)}]) \quad (7)$$

If we consider a fast preequilibrium with a constant K (assuming that the amount of free olefin and CO in solution are not altered by the position of the equilibrium), define $[\mathrm{Ru\text{-}BIAN_{tot}}] = [\mathrm{Ru(CO)_3(Ar\text{-}BIAN)}] + [\mathrm{Ru(CO)_2(olefin)(Ar\text{-}BIAN)}]$ and consider its amount constant (that is, we assume that the equilibrium between $Ru(CO)_3(Ar\text{-}BIAN)$ and $Ru(CO)_5$ is not significantly altered by the formation of some olefin complex, which is acceptable in view of the discussion below), we can write

$$[\mathrm{Ru(CO)_2(olefin)(Ar\text{-}BIAN)}] = (K'\,[\mathrm{Ru\text{-}BIAN_{tot}}][\mathrm{olefin}])/(1 + K'[\mathrm{olefin}]) \quad (8)$$

where $K' = K/[\mathrm{CO}]$. By substitution of eq 8 in eq 7 a kinetic low is obtained that is not in general first order in olefin concentration. However, in case the equilibrium in Scheme 2 were almost completely shifted to the left ($K' \ll 1$), then $[\mathrm{Ru(CO)_3(Ar\text{-}BIAN)}] \cong [\mathrm{Ru\text{-}BIAN_{tot}}]$ and eq 7 reduces to

$$-\mathrm{d}[\mathrm{ArNO_2}]/\mathrm{d}t = [\mathrm{ArNO_2}](k_1 + k_2K'[\mathrm{olefin}])[\mathrm{Ru\text{-}BIAN_{tot}}] \quad (9)$$

which is in perfect agreement with the observed kinetic data. Moreover, the fact that the equilibrium in Scheme 2 should be almost completely shifted to the left is also in agreement with the IR spectra recorded under pressure, in which no cyclohexene complex could be detected. Despite intense effort, we have not yet succeeded in isolating or univocally characterizing an olefin complex of the type $Ru(CO)_2(olefin)(Ar\text{-}BIAN)$.[53] However, the related complex $Ru(CO)_2(i\text{Pr-DAB})(\eta^2\text{-dimethylfumarate})$ is known,[54] and related iron complexes have also been reported.[55]

When a diene was employed as the olefin, a very slow conversion of the initially formed $Ru(CO)_3(Ph\text{-}BIAN)$ to $Ru(CO)_3(\eta^4\text{-}2,3\text{-dimethylbutadiene})$ was observed. This conversion is much slower than the actual catalytic reactions, and the diene complex is unlikely to play any relevant role in it. Moreover, at least in the case of monoolefins, a large amount of evidence indicates that the Ar-BIAN ligand is bound to the metal during the reaction. However, the fact that such a displacement is observed suggests that even with monoolefins the active species may be of the kind $Ru(CO)_3(olefin)(\eta^1\text{-}Ar\text{-}BIAN)$ rather than $Ru(CO)_2(olefin)(\eta^2\text{-}Ar\text{-}BIAN)$, as previously suggested. A palladium complex having a $p\text{-MeOC}_6H_4$-BIAN ligand coordinated in a monodentate fashion has been structurally characterized.[56] The data available at the moment do not allow distinguishing between these two possibilities. In the following we will continue to refer to the active species as having a chelating Ar-BIAN ligand, but the aforementioned ambiguity must be always kept in consideration.

As evident from the data in Figures 2 and 3, the rate of the catalytic reactions is first order in olefin concentration at least up to a 75% fraction of cyclohexene in toluene, but the rate decreases if the neat olefin is used as solvent. The same effect has been observed in other series of reactions (not reported) and is thus a general phenomenon, at least with cyclohexene. This accelerating effect of a small amount of toluene and its leveling off at higher concentrations has intrigued us for some time. Toluene had been selected as a diluting solvent for cyclohexene based on the similarity in polarity between the two. Toluene has a lower dipole moment with respect to that of cyclohexene (0.36 versus 0.55 D, in the gas phase),[57] but a higher dielectric constant (2.379 versus 2.220).[57] However, it turned out that the addition of toluene to a cyclohexene solution of $Ru_3(CO)_{12}$ and the ligand accelerates the formation of $Ru(CO)_3(Tol\text{-}BIAN)$, a transformation that would otherwise take a time not negligible with respect to the total reaction time. It appears that 25% toluene in the solvent is sufficient to render this induction time short enough

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(53) By performing the reaction between $Ru_3(CO)_{12}$ and Ph-BIAN in α-methylstyrene at 160 °C and under 5 bar CO and 10 bar N_2, a complex was obtained showing in the IR spectrum two bands at 2037 and 1973 cm^{-1}, consistent with a species of the aforementioned type. However, this complex proved to be extremely sensitive, and we could not fully characterize it. Use of olefins such as dimethylfumarate or maleic anhydride, successfully employed in the case of reactions of $Ru(CO)_3(i\text{Pr-DAB})$[54] and related iron complexes,[55] in stoichiometric reactions gave complete decomposition of the complex, with loss of all carbonyl absorptions in the IR spectrum.

(54) van Wijnkoop, M.; de Lange, P. P. M.; Frühauf, H.-W.; Vrieze, K.; Smeets, W. J. J.; Spek, A. *Organometallics* **1995**, *14*, 4781.

(55) Frühauf, H.-W.; Pein, I.; Seils, F. *Organometallics* **1987**, *6*, 1613.

(56) Groen, J. H.; Elsevier: C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 3445.

(57) *Handbook of Chemistry and Physics*, 48th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, 1967−1968.

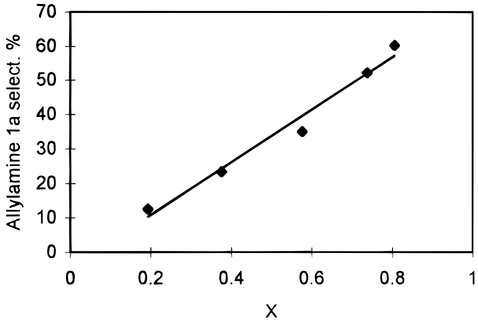

Figure 8. Selectivity in allylamine **1a** as a function of the relative contribution of the process starting from the olefin complex Ru(CO)$_2$(Tol-BIAN)(cyclohexene) with respect to the total reaction (defined as $X = \{\ln([\mathrm{ArNO_2}]_0/[\mathrm{ArNO_2}]_f) - 0.331\}/\{\ln([\mathrm{ArNO_2}]_0/[\mathrm{ArNO_2}]_f)\}$; for the other amounts see the caption to Figure 3) for the reactions described in Figure 2. The straight line passing through the data has the equation Selectivity = $76.7X - 4.57$($R^2 = 0.977$).

that the relative differences in it at higher concentrations become negligible. Although we cannot completely exclude that other small effects on the rate of the reaction are operating (for example a small linear acceleration or retardation of the initial electron transfer may be obscured by the stronger effect of the olefin concentration), all these effects should operate in a proportional way at all concentrations and could not explain the discontinuity observed in the rate law. The higher rate of formation of Ru(CO)$_3$(Ar-BIAN) species in more polar solvents is also evident in the synthesis of **2a** conducted under dinitrogen. In this case, the reaction was about 5 times slower in Decaline than in toluene.

As the equilibrium in Scheme 2 is almost completely shifted to the left, the concentration of Ru(CO)$_3$(Tol-BIAN) can be considered to be constant at different olefin concentrations, and thus even the contribution of the olefin independent term in the rate equation can be considered as constant. This means that the relative contribution of the olefin-dependent process (called X) with respect to the total can be obtained from the equation

$$X = \{\ln([\mathrm{ArNO_2}]_0/[\mathrm{ArNO_2}]_f) - 0.331\}/\ln([\mathrm{ArNO_2}]_0/[\mathrm{ArNO_2}]_f) \quad (10)$$

where [ArNO$_2$]$_0$ and [ArNO$_2$]$_f$ are the nitroarene concentrations at the beginning and at the end of the reaction and 0.331 is the intercept in the rate law. Although the selectivity of the amination reaction and the percentage of olefin in the solvent are not linearly correlated, a good linear correlation exists between the selectivity and the X value calculated in eq 10 (Figure 8).

The linearity of this correlation gives us two important pieces of information. The first is that the selectivity in allylamine for the process starting from the olefin complex is not (or very little) altered by the olefin concentration in solution. In other terms, once the olefin is coordinated to the metal and the resulting complex reacts with the nitroarene, the remaining olefin plays no role. This excludes any process in which a reversible decoordination of the olefin may occur after the reaction with the nitroarene. The second, and more important aspect, is that the intercept at − 4.5 implies that the olefin-independent pathway should have a 4.5% selectivity in allylamine. Within the frame of the experimental errors in the determination of the selectivities (which are sensitive to the error in the determination of both the allylamine and the remaining nitroarene amounts), this number cannot be considered to be precise, but the true value must however be low (actually, it may even be lower than 4.5%). This implies that the reaction starting from Ru(CO)$_3$(Ar-BIAN) in Scheme 2 either does not produce the allylamine at all or does it with only very low yields. This is consistent with the failure to obtain any allylic amine from the reactions of isolated complex **3**, despite the fact that the corresponding allylic amine had been obtained in normal catalytic reactions. Thus complex **3** should not be considered as an intermediate in the synthesis of the allylic amines, but only in the synthesis of the byproducts of the reaction. Interestingly, this also means that even Ru(CO)$_3$(Ar-BIAN) complexes are not a part of the catalytic cycle for the desired product, but only a reservoir for Ru(CO)$_2$-(olefin)(Ar-BIAN) and a source of byproducts. In this context, the lower selectivity obtained with Tol-BIAN with respect to Ph-BIAN can be easily explained as the stronger electron-donating power of the tolyl ligand increasing the reactivity of the tricarbonyl complex, rendering the competition between it and the corresponding olefin complex less selective toward the latter.

As the first act of the reaction is the rate-determining step, the following steps can only be investigated by competition experiments. The most important point is the extent of reduction of the aminating agent at the stage of the coupling with the olefin. Basically, three possibilities exist. The aminating reagent may be an aniline, a nitrosoarene, or an imido (nitrene) fragment. Moreover, in the case of the nitrosoarene, coupling may occur either while the nitrosoarene is coordinated to the metal or while it is free in solution. Precedents exist for all of these possibilities.[58−60]

One experiment conducted with 3,4-dichloronitrobenzene in the presence of unsubstituted aniline afforded only the allylamine derived from the nitroarene, thus clearly indicating that the aniline is not involved in the formation of the allylamine. However, the lower selectivity observed in the presence of added aniline indicates that this compound must be involved in the synthesis of some byproduct.

The identification of the role of nitrosoarene intermediates is less straightforward. The formation of both the allylamine and the hetero Diels−Alder adduct when the reaction is run in the presence of a diene indicates that some coupling must occur at the stage of the nitrosobenzene. Several possibilities are shown in Schemes 3−5.

The easiest explanation is that an initially formed nitrosoarene complex dissociates the organic group and this reacts either with the free diene, to afford the hetero Diels−Alder adduct, or with an olefin complex molecule,

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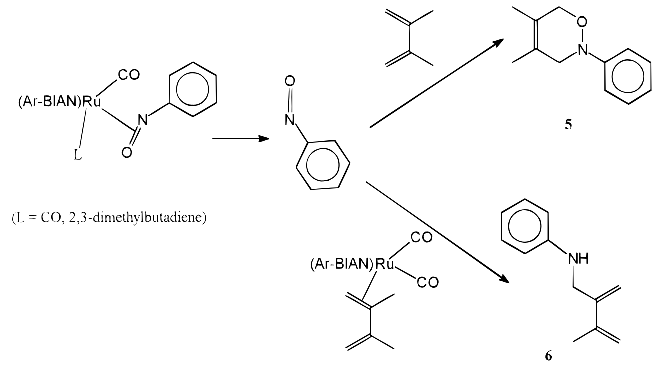
(58) (a) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

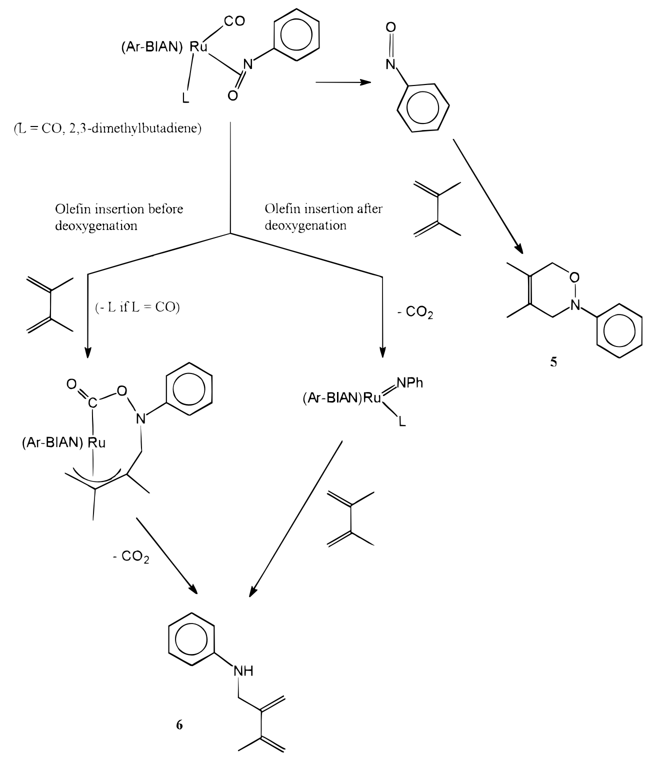
(59) Crotti, C.; Cenini, S.; Bassoli, A.; Rindone, B.; Demartin, F. *J. Mol. Catal.* **1991**, *70*, 175.

(60) (a) Song, J.-S.; Han, S.-H.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2386. (b) Pizzotti, M.; Cenini, S.; Crotti, C.; Demartin, F. *J. Organomet. Chem.* **1989**, *375*, 123.

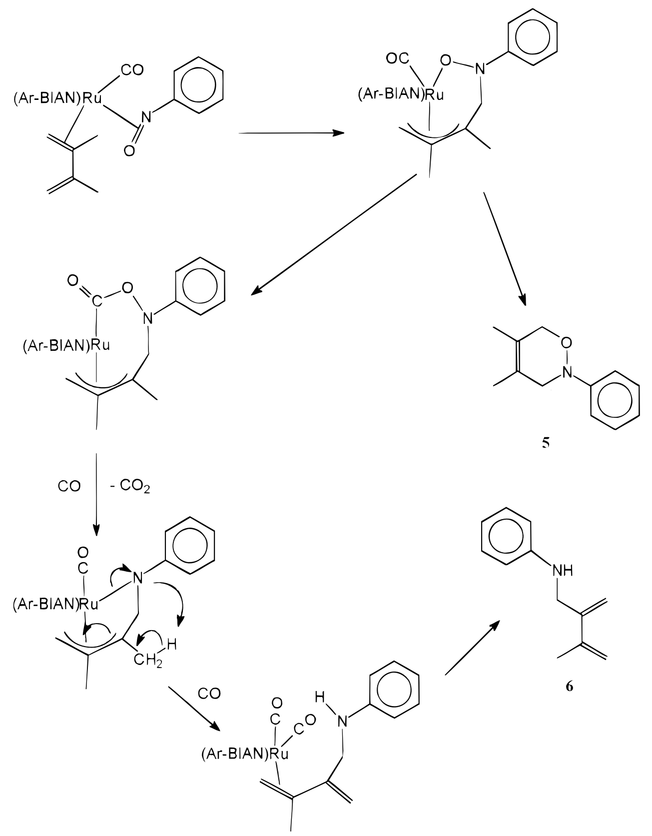
Scheme 3



Scheme 4



Scheme 5



to afford the allylamine. However, this mechanism is inconsistent with the independence of the **5**/**6** ratio from the olefin concentration and (in the case L = CO) even with the rate enhancement at higher olefin concentrations.

Several related mechanisms can be imagined, in which the hetero Diels–Alder adduct derives from an "off metal" reaction of a nitrosoarene irreversibly dissociated from the metal, while the allylic amine derives from a reaction of a coordinated nitrosoarene (Scheme 4). In this last case, coupling with the olefin may precede or follow deoxygenation by CO. In this last eventuality, an imido complex would be the real aminating agent. It should be noted that coupling between a monoolefin and a nitrosoarene in the coordination sphere of a metal has several precedents in platinum chemistry.[61] An example has also been reported of a coupling between a butadiene coordinated to a zirconium or hafnium complex and *t*BuNO.[62] This scenario cannot be completely dismissed and, in case L is the butadiene, is also consistent with the rate dependence, but selectivity independence, of the reaction on the olefin concentration. However, it is unlikely that two such different processes such as dissociation of the nitrosoarene and its coupling with a coordinated ligands showed the same dependency on the temperature from 80 to 160 °C, as experimentally observed. Moreover, the predominance of the hetero Diels–Alder adduct over the allylamine would imply that, during reactions involving cyclohexene, where even the "off metal" process should yield the allylamine, most of the reaction would occur from the free nitrosoarene. This is difficult to reconcile with the fact that nitrosoarene complexes such as **3** do not afford allylamine.

The process in Scheme 5 is consistent with all the experimental facts. In it both **5** and **6** derive from the reactions of a metal-bound nitrosoarene and the reactions pass from a common intermediate. This can then either reductively eliminate **5** or insert CO in the metal–oxygen bond (the oxygen atom of the hydroxylaminato ligand is formally negatively charged and should be nucleophilic) with subsequent elimination of CO_2. Rearrangement of the obtained complex would yield **6**. The scheme would be little altered if the olefin were initially coordinated with both double bonds and/or the Ar-BIAN were coordinated in a monodentate fashion. In the case of cyclohexene, the initially formed

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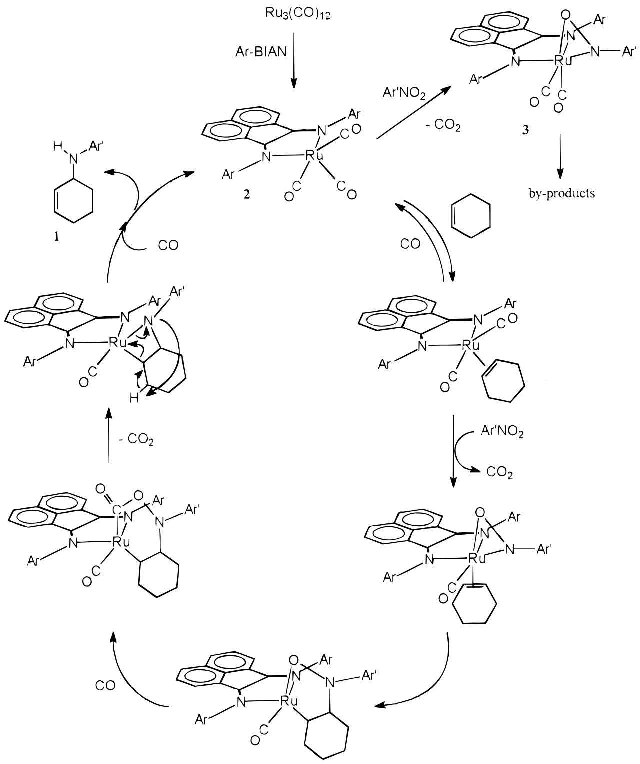
(61) (a) Mansuy, D.; Drême, M.; Chottard, J.-C.; Girault, J.-P.; Guilhem, J. *J. Am. Chem. Soc.* **1980**, *102*, 844. (b) Bellon, P. L.; Cenini, S.; Demartin, F.; Pizzotti, M.; Porta, F. *J. Chem. Soc., Chem. Commun.* **1982**, 265. (c) Cenini, S.; Porta, F.; Pizzotti, M.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1984**, 355. (d) Cenini, S.; Porta, F.; Pizzotti, M.; Crotti, C. *J. Chem. Soc., Dalton Trans.* **1985**, 163. (e) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F.; Masciocchi, N. *J. Organomet. Chem.* **1987**, *330*, 265.

(62) Erker, G.; Humphrey, M. G. *J. Organomet. Chem.* **1989**, *378*, 163.

Scheme 6



coupling product would be unlikely to reductively eliminate an azaoxacyclobutane and would evolve toward the allylamine.

The reaction pathway for cyclohexene, as determined by the discussed data, is reported in Scheme 6. Note that in this case the final step may even proceed by a metal-mediated hydrogen shift, that is, a β-hydrogen elimination followed by reductive elimination of the allylamine.

The formation of an intermediate nitrosoarene complex having also coordinated both an olefin and CO may explain why nitroarenes bearing electron-withdrawing groups not only give higher rates but also afford higher selectivities in allylamine. Indeed, in the coupling with the olefin, the nitrosoarene acts as an electrophile, and these kinds of couplings are known to be accelerated by electron-withdrawing groups on the aromatic ring.[63] 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[31,64] and is the only one occurring when no olefin is present. This reaction will eventually lead to byproducts, but 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.

Conclusions

In this paper we have reported a new catalytic system for the synthesis of allylamines from nitroarenes and unactivated olefins working under CO pressure and involving a formal C−H bond activation. Selectivities are good for several substrates, and the mechanism has been understood at least in its basic features. At the moment, the main limit of the system lies in its decrease in selectivity when higher catalytic ratios are employed, apparently due to the negative effect of the aniline byproduct. The catalytic system, on the other hand, appears to still be active after the end of the reactions even at the highest catalytic ratio employed. This fact is very promising and indicates that this reaction may be rendered more efficient if a way is found to further decrease the amount of aniline formed or to avoid its negative interaction with the catalytic system.

If we compare the present catalytic system with the ones employing phenylhydroxylamine[9−14] or an aniline in the presence of an oxidant,[17] we found that they are partly complementary in their synthetic scope. Our system works the best with nitroarenes containing an electron-withdrawing group, but acceptable yields are obtained even in other cases. The use of hydroxylamines has been up to now limited to phenylhydroxylamine, and for the aniline−oxidant system, the only example we are aware of in which a different aniline was used involved *p*-chloroaniline and gave a very low turnover number (2.4 in 24 h), although the selectivity was high. More interestingly, our system gives good yields with respect to the nitroarene, but requires the use of a very large excess of olefin. On the other hand, systems employing hydroxylamine generally give good yields with respect to the olefin, but several byproducts derived from the aminating agent are observed, so that yields are usually quoted with respect to the olefin. Thus this last synthetic procedure may be preferable when the olefin is a complex molecule and the aminating fragment is simple, while our reaction may be better when the reverse is true. A more in-depth comparison will only be possible when data on more aminating fragments (for the hydroxylamine reaction) and more olefins (for the nitroarene reaction) are available.

Note Added in Proof: After acceptance of this paper, a related article on the allylic amination of olefins by nitroarenes, catalyzed by iron complexes, has been published: Srivastava, R. S.; Nicholas, K. M. *Chem. Commun.* **1998**, 2705.

Experimental Section

General Procedure. Unless otherwise specified, all reactions and manipulations were performed 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. Olefins were purified by distillation over sodium and stored under dinitrogen in the dark 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. Other organic reagents were used as received. $Ru_3(CO)_{12}$[65] and $Ru(CO)_3(DPPE)$[49] were synthesized by methods reported in the literature or slight modifications thereof. All other compounds, except for those mentioned below, were commercial products and were used as received. Gas chromatographic analyses were performed on a Perkin-Elmer 8420 capillary gas chromatograph equipped with a PS

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(63) (a) Hamer, J.; Ahmad, M.; Holliday, R. E. *J. Org. Chem.* **1963**, *28*, 3034. (b) Kresze, G.; Firl, J.; Zimmer, H.; Wollnik, U. *Tetrahedron* **1974**, *20*, 1605.

(64) Note 30 in ref 34.

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255 column. R_i values (R_i = response factor, relative to naphthalene 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 gaschromatograph, equipped with a 5971A mass selective detector. NMR spectra were recorded on a Bruker AC 200 FT (200 MHz) or on a Bruker AC 300 FT (300 MHz) at room temperature. High-pressure IR spectra were recorded by means of a custom-made high-pressure Hastelloy C reactor equipped with IRTRAN 1 (MgF_2) windows and heating and stirring facilities, placed inside a FTS-7 Bio Rad FT-IR spectrometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

Synthesis of the Ligands. Ar-BIAN. The intermediate (Ar-BIAN)$ZnCl_2$ complexes were prepared as reported in the literature.[23,24] Care must be taken to eliminate any residue of the acetic acid employed as solvent in the synthesis, as this has a strongly negative effect on the effectiveness of the separation in the following step. Then 10 mmol of the complex was suspended in CH_2Cl_2 (200 mL) in a separating funnel, and a solution of sodium or potassium oxalate (15 mmol) in water (20 mL) was added. After shaking for 5 min a white precipitate of $Zn(C_2O_4)$ was present, suspended in the aqueous phase. The phases were separated, and the organic layer was washed with water (2 × 20 mL), dried with Na_2SO_4, filtered, and evaporated to dryness, affording the analytically pure ligands in almost quantitative yields (with respect to the intermediate complex). A larger excess of oxalate can also be used, in which case $Zn(C_2O_4)$ is partly solubilized in the aqueous phase as $[Zn(C_2O_4)_2]^{2-}$, but the efficiency of the decomplexation of the Ar-BIAN ligand is not altered. The synthesis of 2,6-$i$$Pr_2C_6H_3$-BIAN was performed by direct reaction of acenaphthene quinone with the amine, without passing through the formation of the zinc complex, as reported in ref 23.

Ph-BIP. Ph-BIP was synthesized in two steps via N,N'-diphenyldiphenylethanediimine. The second step of the reaction was performed as reported in ref 66, but the synthesis of the intermediate product was performed by condensation of aniline with benzil in the presence of molecular sieves, as described in ref 67.

Catalytic Reactions. In a typical reaction, the nitroarene, $Ru_3(CO)_{12}$, and the ligand (see Tables 1−5) were weighed in a glass liner. 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 the solvent 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 reagents 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 was then charged at room temperature at the required pressure, and the autoclave was immersed in an oil bath preheated at the required temperature. Other experimental conditions are reported in Tables 1−5. At the end of the reaction the autoclave was cooled with an ice bath and vented, and the products were analyzed by gas chromatography (naphthalene as an internal standard) or separated by column chromatography on silica.

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**,[68] **1d**,[69] **1e**,[69] **5**,[39] and **6**[14] are known compounds and were identified by their mass spectra and by comparison of the ^1H spectra of the isolated compounds with those reported in the literature and, in the case of **5**, by elemental analysis. The allylamines **1a**−**j** were isolated from the reaction mixtures by column flash chromatography on silica (eluant CH_2Cl_2/hexane). They are all oils and were characterized by their spectroscopic features. After the chromatographic separation, no impurity could be detected in the GC and ^1H NMR spectra of the allylamnines. Thus the purified compounds are evaluated to be at least 98% pure.

1a: ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 1.51−2.21 (m, 6 H, $-CH_2-CH_2-CH_2-$), 3.74 (m, 1 H, $-CH-NH$), 3.90 (s, 1 H, NH), 5.72 (dd, J = 8.2, 2.1 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 5.86 (dd, J = 8.2, 2.1 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 6.42 (dd, J = 9.1, 3.2 Hz, 1 H, Ar−H), 6.68 (d, J = 3.2 Hz, 1 H, Ar−H), 7.16 (d, J = 9.1 Hz, 1 H, Ar−H); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS) δ = 19.64, 25.17, 28.71, 48.06, 112.99, 114.11, 119.35, 127.66, 130.71, 130.95, 132.88, 146.80; MS (70 eV, EI) m/z (%): 241 (35) [M^+], 213 (27) [$M^+ - CH_2CH_2$], 161 (63) [$Cl_2C_6H_3NH_2^+$], 81 (100) [$C_6H_9^+$]; high-resolution mass 241.0432, calcd for $C_{12}H_{13}NCl_2$ 241.0425.

1b: ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 1.58−2.18 (m, 6 H, $-CH_2-CH_2-CH_2-$), 3.15 (s, 1 H, NH), 3.91 (m, 1 H, $-CH-NH$), 5.72 (dd, J = 8.2, 2.5 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 5.92 (dd, J = 8.2, 2.3 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 6.46−6.99 (m, 4 H, Ar−H); m/z (%) 191 (61) [M^+], 1633 (56) [$M^+ - CH_2CH_2$], 111 (100) [$FC_6H_4NH_2^+$], 81 (42) [$C_6H_9^+$].

1f: ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.26−2.34 (m, 10 H, $-CH_2-CH_2-CH_2-CH_2-CH_2-$), 3.75 (s, 1 H, NH), 4.17 (m, 1 H, $-CH-NH$), 5.26 (dd, J = 9.1, 8.1 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 5.78 (dt, J = 9.1, 9.3 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 6.41 (dd, J = 8.8, 2.7 Hz, 1 H, Ar−H), 6.63 (d, J = 2.7 Hz, 1 H, Ar−H), 7.13 (d, J = 8.8 Hz, 1 H, Ar−H); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS) δ = 24.41, 26.72, 27.13, 29.41, 36.60, 51.12, 112.91, 119.61, 131.22, 132.73, 134.18, 147.41; MS (70 eV, EI) m/z (%) 269 (16) [M^+], 226 (62) [$M^+ - C_3H_7$], 187 (26) [$M^+ - C_6H_{10}$], 161 (73) [$Cl_2C_6H_3NH_2^+$], 109 (41) [$C_8H_{13}^+$],67 (100) [$C_5H_7^+$].

1g: ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 1.25−2.49 (m, 4 H, $-CH_2-CH_2-$), 3.72 (s, 1 H, NH), 4.47 (m, 1 H, $-CH-NH$), 5.77 (dd, J = 9.1, 2.2 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 6.01 (dd, J = 9.1, 2.5 Hz, 1 H, $-CH_2-CH{=}CH-CH-$), 6.41 (dd, J = 8.9, 2.9 Hz, 1 H, Ar−H), 6.62 (d, J = 2.9 Hz, 1 H, Ar−H), 7.12 (d, J = 8.9 Hz, 1 H, Ar−H). m/z (%) 227 (24) [M^+], 161 (100) [$Cl_2C_6H_3NH_2^+$], 67 (71) [$C_5H_7^+$].

1j: ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 3.75 (s, 1 H, NH), 4.14 (t, J = 1.8 Hz, 2 H, $-CH_2-$), 5.31 (dd, J = 1.8, 1.6 Hz, 1 H, $=CHH$), 5.51 (d, J = 1.6 Hz, 1 H, $=CHH$), 6.42 (dd, J = 9.0 Hz, 3.0 Hz, 1 H, Ar−H), 6.61 (d, J = 3.0 Hz, 1 H, Ar−H), 7.11 (d, J = 9.0 Hz, 1 H, Ar−H), 7.31−7.53 (m, 5 H, Ar−H); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS) δ = 48.51, 113.31, 114.61, 114.72, 120.41, 126.71, 123.31, 128.82, 131.24, 139.51, 144.62, 148.0; m/z (%) 277 (20) [M^+], 174 (100) [$Cl_2C_6H_3NHCH_2^+$], 115 (15) [$C_9H_7^+$].

Synthesis of Ru(CO)$_3$(Ar-BIAN) (2). Ar = 2,6-iPr$_2$C$_6$H$_3$ (2a). To a 50 mL Schlenk flask equipped with magnetic stirring and a reflux condenser and under a N_2 atmosphere were added $Ru_3(CO)_{12}$ (50.0 mg, 0.078 mmol), 2,6-$i$$Pr_2C_6H_3$-BIAN (117.9 mg, 0.234 mmol), and toluene (10 mL). The solution was refluxed for 4 h, during which the color changed from orange to deep blue-violet and all IR absorptions due to $Ru_3(CO)_{12}$ disappeared. The solution was evaporated to dryness, and the resulting solid was resuspended in n-hexane (5 mL), collected on a filter, and dried in vacuo (128 mg, 80% isolated yield). The reaction can also be performed in Decaline at the same or slightly higher temperature, but the reaction takes about 18 h to reach completion. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.96 (d, $^3J(H,H)$ = 6.9 Hz, 12 H, CH_3), 1.32 (d, $^3J(H,H)$ = 6.9 Hz, 12 H, CH_3), 3.29 (sept, $^3J(H,H)$ = 6.9 Hz, 4 H, CH); 6.16 (d, J = 7 Hz, 2 H, Ar); 7.12 (d, J = 7.9 Hz, 2 H, Ar); 7.28−7.44 (m, 6 H, Ar); 7.55 (d, J = 8.2 Hz,

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2 H, Ar). IR (decaline): $\nu_{CO} = 2044$ (s), 1978 (m), 1972 (m) cm^{-1}. Anal. Calcd for $C_{39}H_{40}N_2O_3Ru$: C 68.20, H 5.87, N 4.08. Found: C 67.84, H 6.06, N 3.80. The compound is very air sensitive, but is stable for several weeks in the solid state and under dinitrogen.

Ar = Ph (2b). To a 50 mL Schlenk flask equipped with magnetic stirring and a reflux condenser and under a N_2 atmosphere were added $Ru_3(CO)_{12}$ (50.0 mg, 0.078 mmol), Ph-BIAN (155.6 mg, 0.468 mmol), and *n*-hexane (10 mL). The solution was refluxed for 30 min, during which the color changed from orange to deep blue-violet, all IR absorptions due to $Ru_3(CO)_{12}$ disappeared, and new absorptions were present at 2049 (s), 1984 (m), and 1975 (m) cm^{-1}. The same outcome is observed if the reaction is performed in toluene. The complex could not be isolated in a pure form due to its extreme air sensitivity and to its very similar solubility properties with respect to the free ligand. The excess ligand could not be extracted with 0.1 N HCl, as reported for the analogous synthesis of $Ru(CO)_3$(*i*Pr-DAB),[29] as Ph-BIAN was completely insoluble in this solvent. Evaporating solutions of **2b** (and also of **2c**) in vacuo leads to decomposition by CO loss, as also reported for $Ru(CO)_3$(*i*Pr-DAB).[54]

Ar = Tol (2c). The procedure is analogous to the one employed for **2a**. IR (*n*-hexane): $\nu_{CO} = 2047$ (s), 1982 (m), and 1974 (m) cm^{-1}. The ^{1}H NMR spectrum after a reaction run in C_6D_6 at 67 °C clearly showed the presence of equimolar amounts of coordinated ($\delta_{Me} = 2.13$) and free ($\delta_{Me} = 2.18$ ppm) ligand, supporting the presence of one molecule of ligand per molecule of complex. The complex could not be isolated in a pure form due to its extreme air sensitivity and to its very similar solubility properties with respect to the free ligand.

Synthesis of $Ru(CO)_2(2,6\text{-}i\text{Pr}_2C_6H_3\text{-BIAN})(\eta^2\text{-}ONC_6H_3\text{-}4Cl,2\text{-}CF_3)$ (3). To a 50 mL Schlenk flask were added $Ru(CO)_3$-(2,6-*i*$Pr_2C_6H_3$-BIAN) (200 mg, 0.29 mmol) and toluene (20 mL), and the solution was cooled at 0 °C with an ice bath. At this temperature was added 4-Cl,2-$CF_3C_6H_3NO_2$ (65.8 mg, 43 μL, 0.29 mmol). The temperature was kept constant and the solution was stirred for 3 h, after which the color of the solution had turned to red-purple, the IR absorptions of **2a** had completely disappeared, and the bands of **3** were the only ones observed in the carbonyl region. The solution was evaporated to dryness at room temperature and the red-purple solid was resuspended in *n*-hexane (5 mL), collected on a filter, and dried in vacuo to afford analytically pure **3** (169 mg, 67% isolated yield). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.71-0.85$ (m, 6 H, CH_3), 0.97 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3); 1.08 (d, ^3J(H,H) = 6.9 Hz, 3 H, CH_3); 1.22−1.29 (m, 6 H, CH_3); 1.38 (d, ^3J(H,H) = 9.6 Hz, 3 H, CH_3); 1.54 (d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3); 2.94 (sept, ^3J(H,H) = 6.8 Hz, 1 H, CH); 3.27 (sept, ^3J(H,H) = 6.9 Hz, 1 H, CH); 3.60 (sept, ^3J(H,H) = 6.6 Hz, 1 H, CH); 3.84 (sept, ^3J(H,H) = 6.6 Hz, 1 H, CH); 6.43 (d, $J = 7.2$ Hz, 1 H, Ar); 6.51 (d, $J = 7.1$ Hz, 1 H, Ar); 7.15−7.59 (m, 11 H, Ar); 7.99 (d, $J = 8.3$ Hz, 2 H, Ar). ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C, $CFCl_3$): $\delta = -65.61$ (s, CF_3). IR (toluene): $\nu_{CO} = 2012$ (s), 1945 (m) cm^{-1}. MS (FAB$^+$): *m/z* 867 (maximum of the multiplet) [M$^+$], 839 [M$^+$ − CO], 811 [M$^+$ − 2CO], 656 [M$^+$ − nitrosoarene]. Anal. Calcd. for $C_{45}H_{43}ClF_3N_3O_3Ru$: C 62.27, H 5.00, N 4.84. Found: C 61.95, H 5.18, N 5.19.

High-Pressure IR Spectra. $Ru_3(CO)_{12}$ (6.39 mg, 0.01 mmol) and the Ar-BIAN ligand in the required amount (see text) were placed in a Schlenk tube under a dinitrogen atmosphere, and the solvent (see text, 10 mL) was added. In several cases, especially when the solvent was hexane, the reagents were not completely soluble. The suspension was then vigorously stirred for 10 min, and 3 mL of the stirred suspension was withdrawn and added to the high-pressure IR cell while purging with dinitrogen. Stirring for prolonged periods or heating must be avoided, as the reaction started in these cases in the Schlenk tube. The cell was closed under dinitrogen and then charged with CO at the required pressure at room temperature.

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