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Metals in Organic Syntheses. IV. A Novel Catalytic Carbonylation Reaction: the Synthesis of Arylamides from 1,3-Diaryltriazenes in the Presence of $PdCl_2(PPh_3)_2$ as Catalyst Precursor

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Our current interest in syntheses with carbon monoxide promoted by metal complexes [1] and in the chemistry of 1,3-disubstituted triazenido transition metal complexes [2] has led us to consider the interaction of these complexes with CO. It has been reported that the hydrido 1,3-di-*p*-tolyltriazenido complex of platinum(II) *trans*-$PtH(dtt)(PPh_3)_2$ undergoes reductive elimination of the triazene molecule Hdtt in reactions with CO to yield $Pt(PPh_3)_2(CO)_2$ and other Pt(0) complexes with triphenylphosphine and bridging carbonyl ligands [1]. Other interesting cases concern reactions in which the triazene ligand is not displaced from the metal. For example, complexes where an acyltriazenido chelating group [C(=O)–N(R)N=NR′] bridges two metals were obtained in reactions of $MX(CO)L_2$ with $HgX'(RN_3R')$ (M = Rh, Ir; X = X′ = halogen or X′ = CF_3COO; L = PR_3) [3]. Acyltriazenido complexes of the type $\{Mo(\pi\text{-}C_5H_5)[Ph(C{=}O)N_3Ph](CO)_2\}$ can be synthesized also by reaction of $Mo(\pi\text{-}C_5H_5)Cl(CO)_3$ with $(PhN_3Ph)^-$ [4]. Another noteworthy case is the reversible CO insertion into Ir–N bond of $Ir(p\text{-}CH_3C_6H_4N\overset{\cdots}{-}N\overset{\cdots}{-}NC_6H_4CH_3\text{-}p)(CO)(PPh_3)_2$ to form the acyltriazenido complex $[Ir\{Ar(C{=}O)N_3Ar\}(CO)_2(PPh_3)]$ [5].

Here it is reported that, in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$, the N=N double bond of the triazene linkage can be replaced by a C=O double bond following reaction (1), with formation of an arylamide:

$$ArNH{-}N{=}NAr + CO \xrightarrow{PdCl_2(PPh_3)_2} ArNH{-}COAr + N_2 \qquad (1)$$

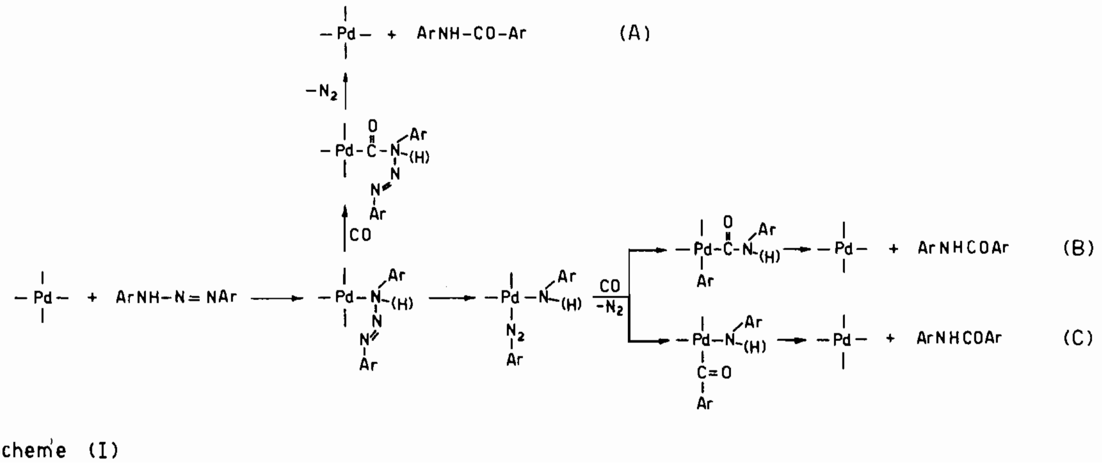
$$Ar = p\text{-}CH_3C_6H_4,\ C_6H_5,\ p\text{-}FC_6H_4,\ p\text{-}ClC_6H_4$$

Carbonylations were carried out in a *ca.* 100 ml stainless steel autoclave; reagents were put in a pyrex bottle placed in the autoclave to prevent any contamination by other metallic species. In a typical experiment 0.05 mmol of $PdCl_2(PPh_3)_2$, 10 ml of solvent (benzene or toluene) and 2 mmol of triazene were treated with carbon monoxide at 100 atm and 100 °C for 8 hr. After cooling and depressurisation, the reaction product was filtered. In the reaction medium the amide is insoluble and can be easily recovered in *ca.* 50% yield. In the remaining solution, other species show N–H and C=O bands (I.R.) but were not further investigated.

Under the above conditions some colloidal palladium forms; this type of decomposition is commonly observed in catalytic carbonylations in the presence of palladium complexes, thus other studies have to be undertaken in order to better understand the nature of the catalytic species.

Reaction (1) is somewhat related to the carbonylation of amines catalyzed by various metal complexes which gives rise to substituted ureas $(RNH)_2CO$, formamides HCONHR, oxamides RHNOC–CONHR, or isocyanates RNCO [6–10].

Reasonable reaction pathways for the catalytic carbonylation of triazene are shown in the scheme. Following pathway (A), CO insertion into a M–N



Scheme (I)

bond yields an acyltriazenido intermediate which leads to the final product after loss of nitrogen.

Alternatively, coordination of the triazene molecule to the metal promotes the N–N fission with formation of an arylamido aryldiazenido intermediate (after formal oxidative addition of ArNH and ArN_2 to some palladium species). Such a type of complexes are well known and, interestingly, aryldiazene complexes can be synthesized by reaction of transition metal complexes with triazenes [11].

Following reaction pathway (B), interaction of CO (possibly coordinated to the metal) with nitrogen of the M–NHAr linkage (or of its deprotonated residue $M–NAr^-$) yields a carbamoyl derivative which ultimately leads to the final product. Carbamoyl intermediates have been proposed in the carbonylation of amines to ureas catalyzed by $Mn_2(CO)_{10}$ [12].

Following reaction pathway (C), after loss of molecular nitrogen with formation of an M–Ar σ-bond, the CO insertion into this bond leads to an aroyl-intermediate similarly to what has been proposed in the carbonylation of diazonium cations to acids (in presence of water) promoted by $Fe(CO)_5$ which occurs *via* a Fe(II)–aryldiazenido carbonyl complex intermediate [13].

Further studies are in progress in order to better understand the nature of the catalytic species, the reaction mechanism, and the possibility to carry out the carbonylation in the presence of metals other than palladium.

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