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ICA Review

Organic Azides and Isocyanates as Sources of Nitrene* Species in Organometallic Chemistry

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1. Introduction

One of the most fascinating fields of organometallic chemistry is concerned with the stabilization of labile organic species by coordination to a transition metal.

More generally, some classes of transition metal complexes appear to be able to generate these species *in situ* from the precursor and under mild conditions. Once formed, they can be trapped on the metal or can give place to a reaction with another ligand bound to the metal or finally they can be involved in a reaction with an organic substrate, sometimes in a catalytic sequence.

Among these species, carbenes have been widely studied as ligands in organometallic complexes and their chemistry is now well developed[1].

On the other hand, much less common appear to be the organometallic derivatives of other important labile organic intermediates such as nitrenes, R–N: (R = alkyl, aryl, sulphonyl *etc.*).

The aim of this review is to describe reactions of organic azides and isocyanates with transition metal complexes, in which these molecules can sometimes behave as sources of nitrene species. It seems thus appropriate to describe also the known, stable nitrene complexes which are in general obtained by different routes.

Derivatives where the R_2N–N: moiety is bound to a metal center will not be considered here.

2. Known Nitrene Complexes

A. Preparation

The best known nitrene complexes involve a metal in a high oxidation state. Their preparation, mainly carried out by Chatt's group, has been readily achieved by reacting a metal oxo derivative with the appropriate source of the NR residue. The first report on this reaction, employing a primary amine as organic reagent, appeared more than ten years ago[2]:

$$OsO_4 + Bu^t\text{–}NH_2 \rightarrow (Bu^t\text{–}N)OsO_3 + H_2O$$

and it was later usefully applied to oxo complexes of rhenium[3–5]:

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* According to IUPAC rules, "imido" should be used instead of "nitrene". However the more familiar term "nitrene" seems to have found widespread acceptance.

$$ReOCl_3L_2 + RNH_2 \rightarrow ReCl_3(NR)L_2 \quad (L = PEt_2Ph, PPh_3; R = aryl)$$

$$Re_2O_3(S_2CNEt_2)_4 + 2PhNH_2 \rightarrow [ReCl(NPh)(S_2CNEt_2)_2]O + 2H_2O$$

In the latter reactions only aromatic amines can be used. In these reactions the Re = O bond behaves as the $>C = O$ bond of aromatic carbonyl derivatives.

Alkylimido rhenium complexes have been obtained by the reactions of $ReOCl_3(PPh_3)_2$ with 1,2-disubstituted hydrazines[6]:

$$ReOCl_3(PPh_3)_2 + RNH\text{–}NHR \cdot 2HCl \xrightarrow{PPh_3} ReCl_3(NR)(PPh_3)_2 + RNH_2 \cdot HCl + O = PPh_3 \quad (R = alkyl)$$

In this case excess of phosphine was employed as the oxygen acceptor. Diarylhydrazines do not react in the same way but RCONHNHPh (R = Me, Ph) give $ReCl_3(NPh)(PPh_3)_2$[6].

Similarly, arylimido molybdenum complexes have been obtained from the reactions of $MoOCl_2(PMe_2Ph)_3$ with $Ar^1CONHNHAr^2$ (Ar^1 = Ph, Ar^2 = Ph, 1-naphthyl, p-$MeOC_6H_4$, p-MeC_6H_4, p-ClC_6H_4)[7]. The products, of formula $MoCl_2(NAr^2)(Ar^1CON_2Ar^2)(PMe_2Ph)$, also contain a chelated 1-aryl-2-aroylazo ligand.

The cation $[ReCl(NMe)(MeNH_2)_4]^{2+}$ has been isolated from K_2ReCl_6, $MeNH_2$, water and oxygen[8], presumably an intermediate rhenium oxo complex being also involved in this reaction.

The reaction of $ReCl_3O(PPh_3)_2$ with phosphinimines, $Ph_3P = NR$, provides an alternative route to the synthesis of nitrene derivatives of rhenium[7]:

$$ReCl_3(NCOPh)(PPh_3)_2 \xleftarrow{Ph_3P=NCOPh} ReCl_3O(PPh_3)_2 \xrightarrow{Ph_3P=NPh} ReCl_3(NPh)(PPh_3)_2$$

and it represents the only way by which rhenium aroylimido complexes can be isolated. However when this reaction was extended to the osmium–oxygen complex, $OsCl_3O(PPh_3)_2$, aryl- instead of aroylimido osmium derivatives were obtained[9]:

$$OsCl_3O(PPh_3)_2 + Ph_3P = NCOC_6H_4X \xrightarrow{-CO} OsCl_2(NC_6H_4X)(PPh_3)_2 \quad (X = H, Cl, OMe)$$

One possible explanation of this decarbonylation reaction is that the phosphinimines decompose to give the nitrenes XC_6H_4CON:, which rearrange to the isocyanates, XC_6H_4NCO.

Further reaction of the formed isocyanates with the oxo complex could give CO_2 and the arylimido complexes. However no reaction was observed between $OsCl_3O(PPh_3)_2$ and PhNCO[9]. On the other hand organic isocyanates do react with other transition metal oxo complexes giving imido derivatives and carbon dioxide[4]:

$$ReCl_3OL_2 + PhNCO \rightarrow ReCl_3(NPh)L_2 + CO_2 \quad (L = PPhEt_2, PPh_3)$$

It should be pointed out that even in the case of rhenium this reaction is not general and in fact $ReClO(S_2CNEt_2)_2$ does not react with PhNCO[5].

It is well known that organic azides, RN_3, are the best source of nitrene residues by means of thermal or photochemical activation,[10] $RN_3 \rightarrow RN: + N_2$. Moreover, copper and copper salts have been successfully used as catalysts for the generation of nitrene intermediates from organic azides[10]. On the basis of this, one could expect that the reaction of an organic azide with an appropriate transition metal complex will produce, at least intermediately, a nitrene complex. However in the reactions so far studied, only by the use of fluorinated azides, could nitrene complexes be isolated[11]:

$$M(PPh_2Me)_4 \xrightarrow{R_FN_3} M(NR_F)(PPh_2Me)_2 \quad (M = Pd, Pt)$$

$$IrCl(CO)(PPh_3)_2 \xrightarrow{R_FN_3} IrCl(NR_F)(CO)(PPh_3)_2$$

$$IrCl(N_2)(PPh_3)_2 \xrightarrow{R_FN_3} IrCl(NR_F)(PPh_3)_2$$

$$Rh(PPh_3)_3Cl \xrightarrow{R_FN_3} RhCl(NR_F)(PPh_3)_2$$

$$M(CO)_3(PPh_3)_2 \xrightarrow{R_FN_3} M(NR_F)(CO)_2(PPh_3)_2 \quad (M = Ru, Os)$$

$$(R_F = CF_3\text{–}CHF\text{–}CF_2)$$

It is noterworthy that in these last reactions the metals are always in an oxidation state lower than in the cases above reported. Presumably displaced phosphines are transformed into the phosphinimino adduct, $R_FN = PR_3$. This is in general the by-product of the reactions between an organic azide and a tertiary phosphine derivative of a transition metal, having more phosphine ligands than the product.

As will be discussed later, the reactions of most organic azides with transition metal complexes in low oxidation states generally lead to a variety of products, but a nitrene complex can only be postulated as intermediate in these reactions.

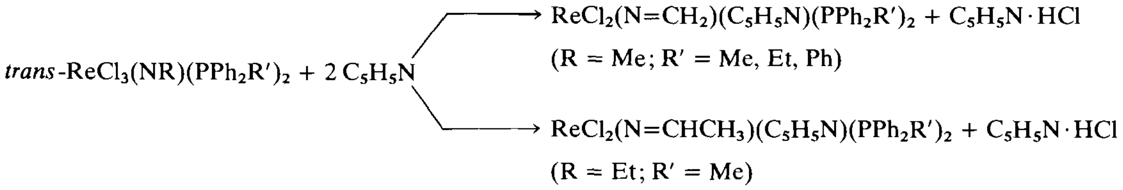
Finally it has been reported that a mononuclear iridium nitrene complex can be obtained by reacting hexafluoroazomethane with a Vaska's type derivative[12a]:

$$2\ trans\text{-}IrCl(CO)(PMePh_2)_2 + CF_3\text{–}N{=}N\text{–}CF_3 \rightarrow 2\ IrCl(NCF_3)(CO)(PMePh_2)_2$$

However non-reproducible molecular weight measurements in solution for this compound do not entirely exclude an alternative dimeric structure[12b].

B. Properties

The most remarkable property of the rhenium nitrene complexes, $ReCl_3(NR)L_2$, (R = alkyl, aryl; L = PR'_3) is their inertness towards N-protonation reaction by using mineral acids[3,6]. On the contrary the protons of the R group (R = CH_3, CH_2CH_3) are acidic enough to give a deprotonation reaction with organic bases[13]:



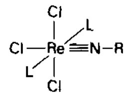
trans-$ReCl_3(NR)(PPh_2R')_2 + 2\,C_5H_5N$

$\rightarrow ReCl_2(N{=}CH_2)(C_5H_5N)(PPh_2R')_2 + C_5H_5N\cdot HCl$ (R = Me; R′ = Me, Et, Ph)

$\rightarrow ReCl_2(N{=}CHCH_3)(C_5H_5N)(PPh_2R')_2 + C_5H_5N\cdot HCl$ (R = Et; R′ = Me)

$ReCl_3(NMe)(PPh_3)_2$ reacts with carbon monoxide giving *cis* and *trans*-$ReCl(CO)_3(PPh_3)_2$ but no evidence of the free nitrene activity was found[13]. Moreover the NR_F residue of the fluoroalkylimido complexes described by Stone[11] did not show any reactivity with CO, CH_3COCl, $HgCl_2$, remaining unchanged in the products. In the i.r. spectra no unambiguous assignements of the M–NR stretching frequencies have been reported for the known nitrene complexes. The arylimido rhenium complexes have rather high dipole moments (*ca.* 4.5–7.5 D)[3], but too low for a *cis* configuration of tertiary phosphine ligands. Thus a *trans* configuration was suggested. The dipole moments decrease with increasing moment of C_{aryl}–X bond (X = Br, Cl, F), suggesting that the nitrene groups lie at the positive end of the dipole, with a positive charge on the nitrogen atom[3].

The metal–nitrogen interaction in these compounds corresponds to a formal triple bond[3]:

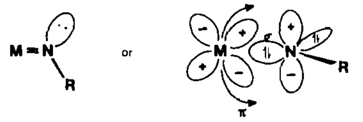


and this accounts for the inertness towards protonation of the nitrene residue bound to the metal. The nitrene ligand thus contributes with four electrons to the bond with the metal and this description of the bond requires an approximatly linear M–N–R arrangement. This has been confirmed by X-ray structure determinations of $ReCl_3(NC_6H_4X)(PEt_2Ph)_2$ (X = OCH_3, $COCH_3$)[14] and $ReCl_3(NMe)(PPh_2Et)_2$[15].

The Re–N bond length is in fact short, but it appears to be slightly dependent of the group attached to N and the overall geometries of these molecules, as much as those of the related nitrido complexes, appear to be strongly influenced by nonbonded interactions[16].

When the metal is in a low oxidation state*, such as in $IrCl(NR_F)(CO)(PPh_3)_2$, although no X-ray structures are known, a more reliable description of the metal–nitrene interaction appears to be related to the now commonly accepted description of the metal–carbon bond in carbene complexes. On considering the nitrogen atom in an ideal sp^2 hybridization, a p_z orbital remains empty and suitable for the π-back donation from the metal to the ligand, superimposed to the σ-donation from one of the sp^2 hybrids of nitrogen. A second hybrid would be filled by a non-bonding lone pairs, while the third hybrid is involved in the bond with the R group.

This description of the metal–nitrene interaction requires a bent M–NR arrangement:



In other words, the metal in these complexes being in a relatively low oxidation state, it is difficult to visualize a nitrene ligand still acting as a four electron donor. The stabilisation of the metal–nitrene bond should be mostly due to the π-back donation from the metal, and this agrees with the fact that the only nitrene complexes of this type which have been reported so far have strong electron withdrawing groups R attached to N.

3. Reactions of Organic Azides with Transition Metal Complexes

A. Reactions in Non-protic Solvents

In Table I, one example of the various types of products which can be obtained by these reactions is reported.

(i) Tetraazadiene derivatives

The first report on the reaction of an organic azide with a transition metal complex leading to a tetraazadiene derivative appeared in 1967[17].

By reaction of MeN_3 with $Fe_2(CO)_9$ in benzene, the stable very volatile orange–red solid $Fe(CO)_3(N_4Me_2)$

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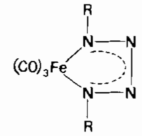
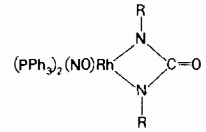
* As far as the contribution to the formal oxidation state of the metal by the nitrene ligand is concerned, we consider that such a ligand does not change the oxidation state, by analogy with carbene complexes[1].

TABLE I. Examples of the Products which can be Obtained from the Reaction of an Organic Azide with a Transition Metal Complex in a Non-protic Medium.

Substrate	R–N$_3$	Solvent	Product	Reference
$Fe_2(CO)_9$	CH_3N_3	C_6H_6		17
trans-$IrCl(CO)(PPh_3)_2$	$C_6H_5CON_3$	$CHCl_3$	$IrCl(PPh_3)_2(RNCO)$	30
$Rh(NO)(CO)(PPh_3)_2$	p-$CH_3C_6H_4SO_2N_3$	C_6H_6		35
trans-$Pt(PEt_3)_2HCl$	$C_6H_5SO_2N_3$	C_6H_6	$Pt(PEt_3)_2Cl(NHR)$	39
$OsH_4(PEtPh_2)_3$	p-$CH_3C_6H_4SO_2N_3$	–	$OsH_2(N_2)(PEtPh_2)_3$	48

was isolated in 20% yield, with other products. This compound represents a remarkable example where an organic compound not stable as a free molecule, that is the tetraazadiene R–N=N–N=N–R, is stabilized by coordination to a transition metal.

Tetraazadiene complexes of cobalt, $(\pi\text{-}C_5H_5)Co(N_4R_2)$, were later synthesized from $(\pi\text{-}C_5H_5)Co(CO)_2$ and RN_3 (R = Me, Ph)[18]. It is noteworthy that the first examples of these compounds are obtained from the reactions or organic azides with a metal carbonyl complex, *i.e.* without involving the carbon monoxide ligand in the reactions. As will be seen later and as one would expect, this ligand is in fact usually attached to the NR residue of the azide.

Tetraazadiene complexes of nickel[12b] and platinum[19] have been obtained from the reactions of organic azides with zerovalent derivatives of these metals:

$$Ni(1,5\text{-}COD)_2 \xrightarrow{RN_3} Ni(1,5\text{-}COD)(N_4R_2) \quad (R = C_6F_5)$$

$$Pt(PPh_3)_4 \text{ or } Pt(PPh_3)_2(C_2H_4) \xrightarrow{RN_3} Pt(PPh_3)_2(N_4R_2) \ (R = C_6H_5SO_2, p\text{–}CH_3C_6H_4SO_2)$$

In these reactions no cycloaddition of the azide to coordinated olefins was observed, as was later confirmed with complexes such as $Pt(PPh_3)_2L$ (L = $CH_2{=}CHCN$, maleic anhydride)[20].

Isoelectronic, formally d^{10} derivatives such as $M(NO)(PPh_3)_3$ (M = Rh, Ir) similarly react with toluene p-sulphonyl azide giving $M(NO)(PPh_3)(N_4R_2)$ (R = p-$CH_3C_6H_4SO_2$)[21]. The latter derivatives are coordinatively unsaturated and readily add a neutral ligand with formation of the corresponding pentacoordinated species, $M(NO)(PPh_3)L(N_4R_2)$ (L = CO, PPh_3, $SbPh_3$)[21].

The nickel and platinum tetraazadiene complexes react with ligands such as PR_3 and CO with substitution of 1,5-COD or PPh_3 respectively, and formation of $Ni(PR_3)_2(N_4R_2)$[12] and $Pt(PPh_3)(CO)(N_4R_2)$[22].

Tetraazadiene complexes have also been obtained by coupling of two diazonium cations on *trans*-$IrCl(CO)(PPh_3)_2$, giving $[Ir(PPh_3)_2(CO)(N_4R_2)]^+(BF_4^-)$ (R = p-XC_6H_4; X = H, F, Cl, Br, CF_3, OCH_3)[23,24].

An unexpected reaction of the tetraazadiene ligand was observed with hydrochloric acid[21]:

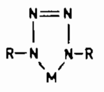
$$Pt(PPh_3)_2(N_4R_2) + 2HCl \rightarrow cis\text{-}Pt(PPh_3)_2Cl_2 + RN_3 + RNH_2$$

$$M(NO)(PPh_3)_n(N_4R_2) + 2HCl \rightarrow M(NO)(PPh_3)_nCl_2 + RN_3 + RNH_2$$

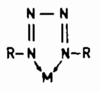
$$(R = p\text{-}CH_3C_6H_4SO_2;\ n = 1,2;\ M = Rh, Ir)$$

At first this behaviour led to the hypothesis that when in solution the chelated tetraazadiene ring lies opened, with formation of nitrene species having the organic azide bound to the metal[21]. Preliminary ^1H n.m.r. studies seemed to support this suggestion. However, further studies on the reactivity, i.r. and ^1H n.m.r. spectra of these compounds at variable temperature ruled out this possibility[22].

The known X-ray structures of tetraazadiene complexes, namely those of $Fe(CO)_3(N_4R_2)$ (R = Me)[25] and $[Ir(PPh_3)_2(CO)(N_4R_2)]^+$ (R = p-FC_6H_4)[24], have shown that the bond between the metal and the tetraazadiene ligand cannot be described by either of the two limiting formulae:



(a)



(b)

This reminds us to the situation reached with butadiene complexes[26]. Formula (a) should correspond to a strong π-back donation from the metal to the ligand which relieves electric charge on the metal and also provides the way for stabilising the tetraazadiene upon coordination. From this point of view, it is noteworthy that the reaction of $Pd(PPh_3)_4$ with RN_3 ($R = p\text{-}CH_3C_6H_4SO_2$) does not lead to the tetraazadiene complex as does the platinum analogue, but instead presumably a polymeric triphenylphosphine derivative of palladium(0) is isolated[27]. This could be due to the less basic character of palladium in respect to platinum[28], which does not allow a stabilisation of the tetraazadiene ligand through the π-back donation mechanism.

In the 4000–650 cm^{-1} region of the i.r. spectra, no bands can be obscrved clearly attributable to the N_4R_2 moieties, and only the characteristic absorptions of the R group can be detected.

(ii) Isocyanate derivatives

It is well known that the reaction of an organic azide with carbon monoxide leading to the formation of the corresponding isocyanate requires rather drastic conditions[10,29]. However, when carbon monoxide is bound to a transition metal, this reaction proceeds under very mild conditions. In this way isocyanate complexes of iridium[30], rhenium[31] and ruthenium[20] have been obtained:

$$trans\text{-}IrCl(CO)(PPh_3)_2 \xrightarrow{RN_3} IrCl(PPh_3)_2(RNCO)$$
$$(R = C_6H_5CO,\ 2\text{-carbonylfuran},\ etc.)$$

$$Re(NO)(CO)_2(PPh_3)_2 \xrightarrow{RN_3} Re(NO)(CO)(PPh_3)_2(RNCO)\ (R = C_6H_5CO,\ p\text{-}CH_3C_6H_4CO)$$

$$Ru(CO)_3(PPh_3)_2 \xrightarrow{RN_3} Ru(CO)_2(PPh_3)_2(RNCO)$$
$$(R = C_6H_5CO,\ p\text{-}CH_3C_6H_4CO,\ p\text{-}CH_3C_6H_4SO_2)$$

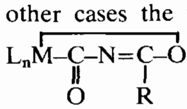
This reaction parallels the formation of –M–NCO derivatives from carbon monoxide and an azido complex, $–M–N_3$, and more closely from a carbonyl derivative and the N_3^- ion[32]. Even in these cases the experimental conditions are mild. The isolation of the iridium complexes requires the use of a solvent such as ethanol-free chloroform. In fact, if ethanol is present, the isocyanate is transformed into the corresponding urethane, while the iridium can be recovered as the dinitrogen complex, $IrCl(PPh_3)_2(N_2)$.

The kinetics for these reactions have also been studied and it has been found that electron withdrawing substituents on the azide accelerate the reaction, suggesting that the azide behaves as an electrophile in the rate determining step[30]. This is also supported by the fact that alkylated phosphines as ligands in the starting iridium complex make the reaction faster than in the case of the triphenylphosphine derivative. Although the homologous rhodium dinitrogen complex could not be isolated in this work from the reaction of $RhCl(CO)(PPh_3)_2$ and RN_3, kinetic measurements have shown that the rates of reactions of the iridium complexes are generally 1.4 to 2.2 times faster than those of the corresponding rhodium complexes. Low enthalpies (*ca.* 6.7–8.8 kcal/mol) and large negative entropies (–34 to –42 e.u.) of activation were calculated and they are consistent with a bimolecular reaction.

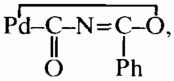
With a very reactive azide such as $p\text{-}CH_3C_6H_4SO_2N_3$, the isolation of the ruthenium isocyanate complex, $Ru(CO)_2(PPh_3)_2(RNCO)$, is possible only if the reaction medium is kept to 0–5° C[20]. At higher temperatures the reaction is more complex (see 3. (iii)).

The presence of the isocyanate ligand in these compounds has been confirmed by their reactivity with respect to protonation reactions. In fact once coordinated to a metal, the isocyanate ligand can be easily protonated with mineral acids leading to the cationic carbamoyl complexes $[Re(NO)(CO)(PPh_3)_2(CONHR)]^{+}$[31] and $[Ru(CO)_2(PPh_3)_2(CONHR)]^{+}$[20] ($R = C_6H_5CO$). For $R = p\text{-}CH_3C_6H_4SO_2$, this type of derivatives could not be obtained, and by reaction of $Ru(CO)_2(PPh_3)_2(RNCO)$ with HBF_4 the organic ligand is displaced as the corresponding sulphonyl amide, RNH_2, with loss of carbon monoxide from the –NCO group. With a weak acid such as ethanol the same reaction takes place; in this case the carbon monoxide displaced from the –NCO group still remains in the coordination sphere of the metal, which can be isolated as $Ru(CO)_3(PPh_3)_2$[20].

In the case of *trans*-$IrCl(PPh_3)_2(RNCO)$ (R = furoyl), the reaction with ethanol gives RNHCOOEt, RNH_2 and *trans*-$IrCl(CO)(PPh_3)_2$, with carbon monoxide abstraction from the ethanol. On the other hand, while the rhenium derivative with $R = C_6H_5CO$ is inert to ethanol[31], the ruthenium complex ($R = C_6H_5CO$) gives place to an unidentified product still containing the organic ligand[20]. However in these cases a different type of metal–isocyanate bond seems to be extant.

Infrared spectroscopic evidence has in fact shown that while in the iridium complexes and in $Ru(CO)_2(PPh_3)_2(RNCO)$ ($R = p\text{-}CH_3C_6H_4SO_2$) the metal is bound to the –N=C– bond of the organic ligand[20,30], in other cases the formation of a metallocycle such as  $L_nM{-}\underset{\underset{O}{\|}}{C}{-}N{=}\underset{\underset{R}{|}}{C}{-}O$ is more consistent with the stability and the i.r. absorptions of these derivatives which in any case do not show any band at about 2200 cm^{-1} as thc free isocyanate ligand. Instead bands below 1650 cm^{-1} were observed. Similarly the recently reported X-ray structure of an analogous metallocycle in $Pt(PPh_3)_2$

$(PhCON{=}NCOPh)\cdot C_2H_5OH$, has ruled out a coordination through the $-N{=}N-$ double bond of the dibenzoylazo ligand[3a]. The number of known metallocycles of this type has recently increased substantially. Moreover metallocycles similar to those proposed for the rhenium and ruthenium complexes[20,30], have been postulated for the compounds obtained directly from the reactions of benzoyl isocyanate with Pd(bipyridine) (dibenzylideneacetone), which gave (bipyridine)

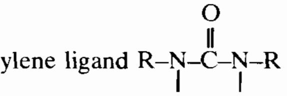


$\underset{\underset{O}{\|}}{Pd\text{–}C}\text{–}N{=}\underset{\underset{Ph}{|}}{C}\text{–}O$, or with $Rh(PPh_3)_3Cl$ and subsequent reaction of the product with bipyridine and $NaBPh_4$[33b].

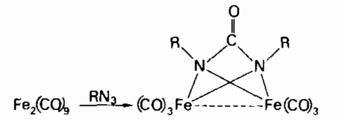
The compound isolated from the reaction between $Rh(PPh_3)_3Cl$ and PhCONCO was shown to be $[RhCl(PPh_3)_2(PhCONCO)]_2$, a rhodium complex having the isocyanate ligands bridging the two metal atoms.

(iii) Ureylene derivatives

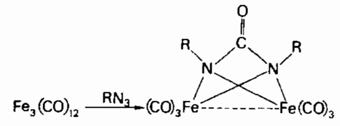
The reactions of organic azides RN_3 with a metal carbonyl complex result in most cases in the formation of derivatives where the ureylene ligand



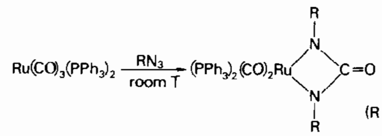
$R\text{–}\underset{|}{N}\text{–}\overset{\overset{O}{\|}}{C}\text{–}\underset{|}{N}\text{–}R$ is present. Both dimeric[17,34] and monomeric[20,35] derivatives of this type have been isolated:



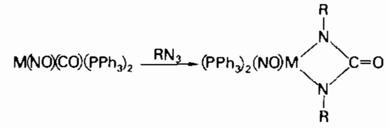
(R = Me, Ph)



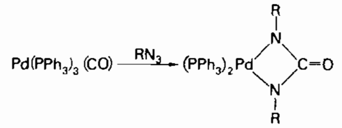
(R = Ph, p-$CH_3OC_6H_4$)



(R = p-$CH_3C_6H_4SO_2$)

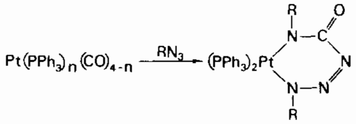


(M = Rh, Ir, R = p-$CH_3C_6H_4SO_2$)

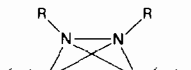


(R = p-$CH_3C_6H_4SO_2$)

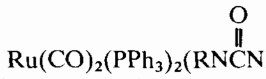
The same reaction carried out on $Pt(PPh_3)_n(CO)_{4-n}$ (n = 2.3) leads to the isolation of a more complex compound[35]:



Besides the reported formulation, other structures seem possible for this derivative[35], which in any case could represent the precursor which by loss of nitrogen can give place to the monomeric ureylene derivatives. However the iron complexes seem to originate from the spontaneous rearrangement in solution of derivatives such as[17].

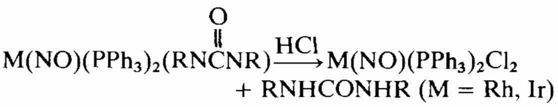


This could be also the case for the ruthenium complex,

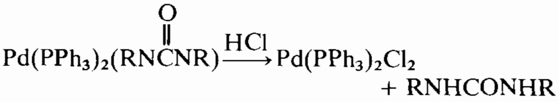


$Ru(CO)_2(PPh_3)_2(RN\overset{\overset{O}{\|}}{C}NR)$, but in this latter case further reaction of the azide with the initially formed isocyanate complex $Ru(CO)_2(PPh_3)_2(RNCO)$, can also provide a reaction path leading to the chelated ureylene derivative[20].

The ureylene ligand is readily displaced from the complexes by mineral acids:

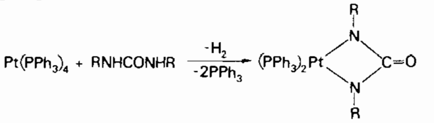


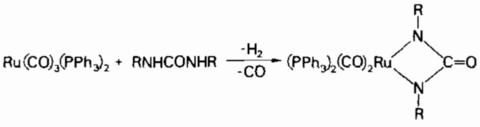
$$M(NO)(PPh_3)_2(RN\overset{\overset{O}{\|}}{C}NR)\xrightarrow{HCl}M(NO)(PPh_3)_2Cl_2 + RNHCONHR\ (M = Rh, Ir)$$

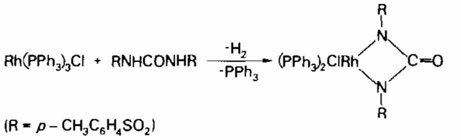


$$Pd(PPh_3)_2(RN\overset{\overset{O}{\|}}{C}NR)\xrightarrow{HCl}Pd(PPh_3)_2Cl_2 + RNHCONHR$$

On the other hand some of the compounds reported above and other related derivatives can be synthesized by oxidative addition of toluene p-sulphonyl urea to the appropriate substrate[20,35].







(R = p-$CH_3C_6H_4SO_2$)

These reactions unambiguously confirmed the nature of the monomeric ureylene derivatives, which show in the i.r. spectra a characteristic absorption due to the carbonyl group of the urea at about 1680–1690 cm^{-1}.

The X-ray structure of the μ-dimethylureylenebis(tricarbonyliron) synthesized by Knox[17] has also been determined[36].

(iv) Amido and imino derivatives

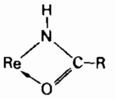
The reactions of organic azides RN_3 with hydrido derivatives of tin such as R'_3SnH are known to give imino, R'_3SnNHR ($R = Ph$; $R' = Me$)[37], or amido derivatives ($R = PhCO$; $R' = Bu^n$);[38] the latter are readily hydrolyzed by water with formation of benzamide. These reactions have also been studied with some transition metal monohydride complexes. A series of amido and imino derivatives of platinum have been isolated according to the reaction:[39]

$$trans\text{-}Pt(PR_3)_2HX \xrightarrow{R'N_3} Pt(PR_3)_2(X)(NHR')$$

(R = alkyl or aryl; X = halogen or pseudo-halogen; $R' = RSO_2, RCO, RCO_2, R$). Amido complexes of rhenium have been analogously obtained[40]:

$$Re(CO)_2(PPh_3)_3H \xrightarrow{RN_3} Re(CO)_2(PPh_3)_2(NHR)$$
$$(R = C_6H_5CO, p\text{-}CH_3C_6H_4CO)$$

These compounds have probably the carbonyl group of the amido ligand involved in the coordination with the metal:



This hypothesis arises both from i.r. evidence (no absorptions in the usual ketonic region) and from their stability which should be unusual for pentacoordinated rhenium(I) compounds[40]. A similar type of bonding has been proposed for related amido complexes obtained by other routes[41].

It should be noted that in one case, that is with $RhH(DPE)_2$ and $p\text{-}CH_3C_6H_4SO_2N_3$, the dimeric complex $(DPE)_2Rh(RN\text{–}NR)Rh(DPE)_2$ ($DPE = Ph_2P\text{–}CH_2CH_2\text{–}PPh_2$), probably having a di-imide bridge and not the expected amido complex, has been obtained[35].

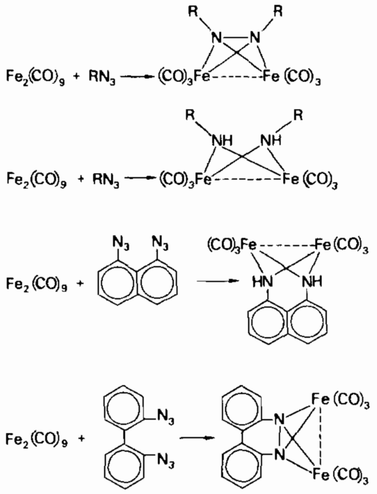
The synthesis of amido complexes from this type of reaction appears to be limited to monohydrido derivatives. With polihydrides the reaction leads to different products (see next section).

(v) Other products

We have already reported the reactions which lead to the isolation of nitrene complexes even when carbon monoxide is bound to the metal (section 2. A).

In some cases the reaction of an organic azide with a transition metal carbonyl complex can lead to other types of products with non-involved carbon monoxide:

$$Ru_3(CO)_{12} + R_FN_3 \rightarrow Ru_3(CO)_9(NR_F)_2$$
$$(R_F = CF_3CHFCF_2)^{11}$$

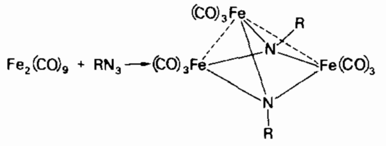

(R = Ph) (17)

(R = Ph, Me) (17)

(ref. 42)

(ref. 42)

The formation of derivatives in which a NR residue is triply bridged has also been observed:


(R = Me) (17)

$$Fe_2(CO)_9 + Me_3SiN_3 \rightarrow Fe_3(CO)_{10}(NSiMe_3)$$
(ref. 43; x-ray: ref. 44)

From the reaction of cobalt carbonyl and phenyl azide no organometallic derivatives could be obtained[45]. Trimethylsilylazide has been also employed for the synthesis of a molybdenum nitrido complex[46]. In particular cases dinitrogen derivatives can be obtained:

$$MCl(CO)(PPh_3)_2 + RN_3 \rightarrow MCl(N_2)(PPh_3)_2$$
$$(M = Rh, Ir; R = C_6H_5CO, \text{furoyl})^{30,47}$$

$$OsH_4(PEtPh_2)_3 + RN_3 \rightarrow OsH_2(N_2)(PEtPh_2)_3$$
$$+ RNH_2\ (R = p\text{-}CH_3C_6H_4SO_2)^{48}$$

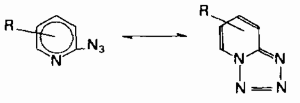
The iridium dinitrogen complex can be isolated only using chloroform stabilized with ethanol as solvent[30]; by this way the organic isocyanate initially formed is transformed into RCONHCOOEt. In the absence of ethanol, isocyanate complexes were isolated (3. A. (ii)).

The synthesis of the osmium dinitrogen complex from OsH_4L_3 and RN_3 probably proceeds *via* the amido complex (3. A. (iv)). However, the presence in the starting material of other hydridic hydrogens leads to the displacement of the amido ligand as the corresponding amide[48].

A peculiar reaction has been observed by reacting $MoCl_4(PPr^nPh_2)_2$ and toluene p-sulphonylazide[49]:

$$2\,MoCl_4(PPr^nPh_2)_2 + 2\,p\text{-}MeC_6H_4SO_2N_3 \rightarrow 2\,MoCl_4(-N{=}PPr^nPh_2)(O{=}PPr^nPh_2) + p\text{-}MeC_6H_4S{-}SO_2C_6H_4Me\text{-}p + 2\,N_2$$

The organic chemistry of 2-pyridyl azides (Py–N_3) has shown that these molecules are in equilibrium with the corresponding tetrazole derivatives[10].



For R = H this equilibrium lies to the right. The reactions of 2-pyridyl azide with complexes such as $Ni(PPh_3)_2Cl_2$, $Pd(PhCN)_2Cl_2$ and $Ru(PPh_3)_3Cl_2$ have been studied[40]. However the products have the azide coordinated in its tetrazole form; the ruthenium derivative, $Ru(PPh_3)_2(Py{-}N_3)_2Cl_2$, reacts with carbon monoxide but only substitution of one tetrazole ligand by CO takes place.

Finally it has been reported that the reactions of $M(PPh_3)_4$ complexes (M = Pd, Pt) with RN_3 (R = Me, Et) in benzene give $M(PPh_3)_2(N_3)_2$[50]. This is a remarkable reaction since there occurs breaking of the R–N_3 bond of the azide. This breaking leading to azido derivatives is usually observed when protic solvents are used (3.B), while in non-polar solvents such as benzene the NR residue of the azide is generally involved in the reaction. However, the nature of the R groups plays a relevant role in determining the kind of products that can be isolated. Further example is the reaction of $Fe_2(CO)_9$ with MeN_3 from which $Fe(CO)_3(N_4Me_2)$ can be obtained (3. A. (i)), while, by using sulphonyl azides, derivatives having all the carbonyl groups displaced and bridged ureas $R{-}SO_2{-}\underset{|}{N}{-}CO{-}\underset{|}{N}{-}SO_2{-}R$ as ligands have been isolated[51].

B. Reactions in Protic Solvents

In Table II, one example of the various types of products which can be obtained by these reactions are reported.

(i) Amido derivatives

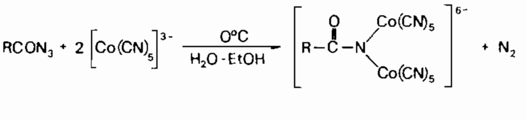
The organic azides RSO_2N_3 and $RCON_3$ (R = aryl) react with complexes of zerovalent palladium and platinum in solvents such as ethanol or wet benzene yielding the corresponding amido derivatives:

$$Pt(PPh_3)_n + RSO_2N_3 \rightarrow Pt(PPh_3)_2(X)(NHSO_2R)$$
$$(n = 3,4;\ X = OH, N_3, NHSO_2R;\ R = Ph, p\text{-}CH_3C_6H_4)^{19}$$

$$Pd(L{-}L)(dba) + RN_3 \rightarrow Pd(L{-}L)(X)(NHR)$$

(R = p-$CH_3C_6H_4CO$, X = N_3, L–L = 2,2′-bipyridyl; R = p-$CH_3C_6H_4SO_2$, X = NHR, L–L = 2,2′-bipyridyl or o-phenanthroline)[20].

The amido complex, $Ru(CO)_2(PPh_3)_2(NHCOR)_2$ (R = furyl), has been obtained by reacting $Ru(CO)_3(PPh_3)_2$ with furoyl azide in benzene, probably because of the presence of adventitious moisture[20]. A cobalt complex having a bridging amido group has also been reported[52]:



(ii) Carboxamido derivatives

Carboxamido (or carbamoyl) derivatives of transition metals are usually obtained by the nucleophilic attack of aliphatic amines on a cationic carbonyl complex[53]. These compounds have been also obtained from the reactions of organic azides such as $RCON_3$ (R = aryl) with a nitrosyl carbonyl complex of rhenium[31]:

$$Re(CO)_2(NO)(PPh_3)_2 + RCON_3 \xrightarrow{C_2H_5OH} Re(NCO)(NO)(PPh_3)_2(CONHCOR) + 2\,N_2 + 2\,RCOOC_2H_5$$

(R = C_6H_5, p-$CH_3C_6H_4$)

TABLE II. Examples of the Products which can be Obtained from the Reaction of an Organic Azide with a Transition Metal Complex in Protic Solvents.

Substrate	R–N_3	Solvent	Product	Reference
$Pt(PPh_3)_3$	p-$CH_3C_6H_4SO_2N_3$	EtOH	$Pt(PPh_3)_2(N_3)(NHR)$	19
$Re(CO)_2(NO)(PPh_3)_2$	p-$CH_3C_6H_4CON_3$	EtOH	$Re(NCO)(NO)(PPh_3)_2(CONHR)$	31
$Pt(PPh_3)_3(CO)$	p-$CH_3C_6H_4SO_2N_3$	EtOH	$Pt(PPh_3)_2(N_3)(-\underset{\underset{R}{\mid}}{N}-COOEt)$	35
$Pt(PPh_3)_2(CO)_2$	p-$CH_3C_6H_4SO_2N_3$	EtOH	*trans*-$Pt(PPh_3)_2(COOEt)_2$	35
$Pt(PPh_3)_4$	$C_6H_5CON_3$ or $EtOC(O)N_3$	EtOH	$Pt(PPh_3)_2(N_3)_2$	19

These compounds undergo an interesting isomerisation when in chloroform solution, a terminal carbonyl ligand being generated from the carbamoyl group, yielding the corresponding amido complexes[31]:

$$\mathrm{Re(NCO)(NO)(PPh_3)_2(CONHCOR)} \xrightarrow{\mathrm{CHCl_3}} \mathrm{Re(NCO)(NO)(PPh_3)_2(CO)(NHCOR)}$$

Carbamoyl complexes have also been obtained by protonation with mineral acids of isocyanate derivatives (3. A. (ii)). However, on reacting the rhenium complex, $\mathrm{Re(CO)(NO)(PPh_3)_2(RCONCO)}$, with hydrochloric acid, an isomer of probable formula $\mathrm{[Re(CO)(NO)(PPh_3)_2\{C(OH){=}NCOR\}]^+Cl^-}$ has been isolated[31]. This derivative should correspond to the intermediate proposed during the formation of carbamoyl complexes by hydroxide addition to coordinated isocyanide ligands[54].

(iii) Other products

The reactions of carbonyl phosphine complexes of platinum(0) in alcohols with toluene *p*-sulphonyl azide gives place to products having esther groups bound to the platinum atom or to the NR residue of the azide:[35]

$$\mathrm{Pt(PPh_3)_2(CO)_2} \xrightarrow[\mathrm{RN_3}]{\mathrm{R'OH}} trans\text{-}\mathrm{Pt(PPh_3)_2(COOR')_2}$$

$$(\mathrm{R'} = \mathrm{Me, Et};\ \mathrm{R} = p\text{-}\mathrm{CH_3C_6H_4SO_2})$$

$$\mathrm{Pt(PPh_3)_3(CO)} + \mathrm{RN_3} \xrightarrow{\mathrm{R'OH}} \mathrm{Pt(PPh_3)_2(N_3)(-\underset{\underset{\displaystyle R}{|}}{N}-COOR')}$$

$$(\mathrm{R'} = \mathrm{Et, Pr^n};\ \mathrm{R} = p\text{-}\mathrm{CH_3C_6H_4SO_2})$$

For $\mathrm{Pt(PPh_3)_2(COOEt)_2}$ an X-ray structure determination has confirmed the *trans* configuration for this complex[55]. When $\mathrm{Pt(PPh_3)_2(-\underset{\underset{\displaystyle R}{|}}{N}-COOEt)}$ was decomposed with hydrochloric acid, *cis*-$\mathrm{Pt(PPh_3)_2Cl_2}$ and an organic material were recovered; the latter was shown to be p-$\mathrm{CH_3C_6H_4SO_2NHCOOEt}$ by elemental analysis, i.r., ^{1}H n.m.r. and mass spectra.

The reactions in alcohol of $\mathrm{Pt(PPh_3)_4}$ with $\mathrm{RCON_3}$ (R = Ph, p-$\mathrm{NO_2C_6H_4}$, OEt) gave only $\mathrm{Pt(PPh_3)_2(N_3)_2}$[19]. With p-$\mathrm{CH_3C_6H_4SO_2N_3}$, $\mathrm{Pt(PPh_3)_2(N_3)(SO_2C_6H_4CH_3}$-$p)$ could be isolated[19], besides $\mathrm{Pt(PPh_3)_2(N_3)(NHSO_2C_6H_4CH_3}$-$p)$ (3. B. (i)). The ethylene adduct, $\mathrm{Pt(PPh_3)_2(C_2H_4)}$, reacts with liquid azides $\mathrm{RCON_3}$ (R = $\mathrm{OBu^t}$, OEt) leading to the formation of $\mathrm{Pt(PPh_3)_2(NCO)(N_3)}$, *via* a carbon monoxide abstraction from the azide.

4. Reactions of Organic Isocyanates with Transition Metal Complexes

Since these organic reagents are sensitive to protic media, inert solvents such as dry benzene are always used. In Table III, one example of the various types of products which can be obtained by these reactions is reported.

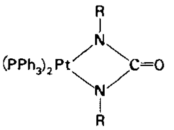
A. Isocyanate Derivatives

There are few reports on the reactions of an organic isocyanate with transition metal derivatives giving isocyanate complexes, *e.g.*[30,33b,56]:

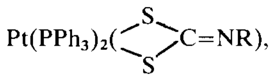
$$\mathrm{IrCl(N_2)(PPh_3)_2} + \mathrm{RNCO} \rightarrow \mathrm{IrCl(PPh_3)_2(RNCO)} + \mathrm{N_2}$$

$$(\mathrm{R} = p\text{-}\mathrm{CH_3C_6H_4CO})$$

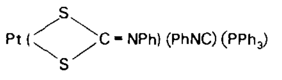
TABLE III. Examples of the Products which can be Obtained from the Reaction of an Organic Isocyanate with a Transition Metal Complex.

Substrate	RNCO	Product	Reference
$\mathrm{Rh(PPh_3)_3Cl}$	PhNCO	$\mathrm{Rh(PPh_3)_2(RNCO)_2Cl}$	56
$\mathrm{Pt(PPh_3)_4}$	p-$\mathrm{CH_3C_6H_4SO_2NCO}$		35
$\mathrm{Ti(NMe_2)_4}$	PhNCO	$\mathrm{Ti(-\underset{\underset{\displaystyle Ph}{|}}{N}CONMe_2)_4}$	63
$(\pi$-$\mathrm{C_5H_5)W(CO)_3H}$	MeNCO	$(\pi$-$\mathrm{C_5H_5)W(CO)_3(CONHR)}$	65
$\mathrm{Ru_3(CO)_{12}}$	PhNCO	$\mathrm{Ru_3(CO)_{10}NR}$	67

$$Rh(PPh_3)_3Cl + 2PhNCO \rightarrow Rh(PPh_3)_2(PhNCO)_2Cl + PPh_3$$

Phenyl isothiocyanate when reacted with $Rh(PPh_3)_3Cl$ gave a similar product, having both π-bonded and donor coordinated isothiocyanates[57]. In this latter case, the π-coordination probably involves the $-C{=}S$ bond of the organic ligand. The same type of coordination has been proposed for the complexes $Pt(PPh_3)_2(RNCS)$ (R = Me, Ph) obtained from $Pt(PPh_3)_3$ and $RNCS$[57]. More complex products, that is  were isolated by conducting the reaction in the presence of an excess of the ligands, probably *via* the non-isolable $Pt(PPh_3)_2(RNCS)_2$[58].

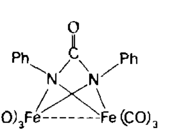
Sulphur abstraction leads to the products with concomitant formation of the corresponding isocyanide RNC; in fact from the reaction mixture the complex



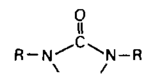
has also been isolated[58]. Abstraction of sulphur or oxygen from isothio- and isocyanates by metal carbonyl complexes leading to isocyanide derivatives has been observed many years ago[59]. In the latter work the synthesis of isocyanate complexes from the reaction of $Fe_3(CO)_{12}$ with RNCO was reported; however the obtained complexes were later shown to be ureylene derivatives (4. B.). The nickel isocyanate complex $[Ni(Bu^tNCO)]_n$ has been isolated by treating $Ni(Bu^tNC)_2(O_2)$ with Bu^tNCO in toluene at room temperature, while the reaction between $Ni(Bu^tNC)_2$ and Bu^tNCO gave a compound of probable stoichiometry $Ni(Bu^tNC)_2(Bu^tNCO)$[60]. Strangely enough, in these complexes the i.r. absorptions of the isocyanate ligand are not markedly affected by coordination to the zero-valent nickel atom.

B. Ureylene Derivatives

The reactions of RNCO (R = Bu^n, Ph) with $Fe_3(CO)_{12}$ led to compounds which were first formulated as $Fe_2(CO)_6(PhNCO)_2$[59]. However an X-ray structure determination of the phenyl derivative has shown that this compound is in fact the μ-diphenyl-ureylene-bis(tricarbonyl iron) complex[61]:

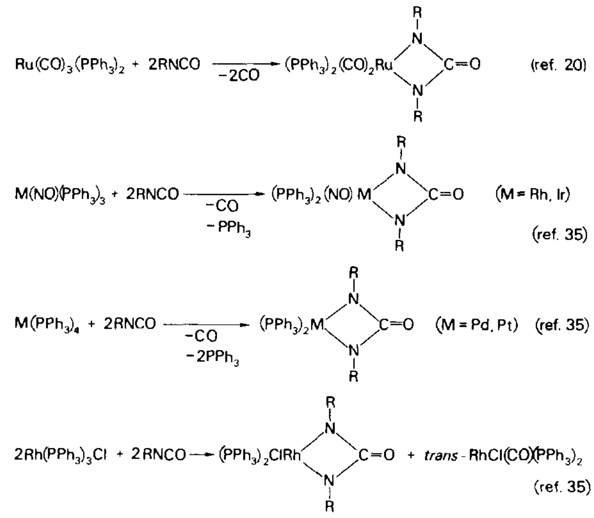


Similarly, the reaction of $Fe_2(CO)_9$ with MeNCO leads to the corresponding methyl derivative[17]. Complexes having chelated ureylene ligand,



(R = p-$CH_3C_6H_4SO_2$)

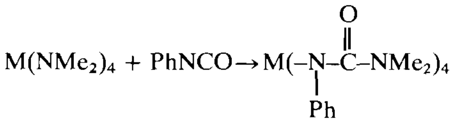
have been obtained according to the following reactions:[20,35]



The synthesis of the rhodium ureylene complex leads also to the isolation of *trans*-$RhCl(CO)(PPh_3)_2$. In this reaction carbon monoxide abstraction takes place probably because of the known effective capacity of $Rh(PPh_3)_3Cl$ to behave as a decarbonylating agent[62].

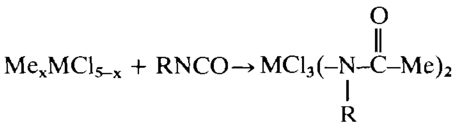
C. Amido and Carboxamido Derivatives

Amido derivatives have been isolated by the insertion reactions of organic isocyanates into the metal–nitrogen[63] and metal–carbon[41] bonds:



$$M(NMe_2)_4 + PhNCO \rightarrow M(-N(Ph)-C(=O)-NMe_2)_4$$

(M = Ti, Zr, Hf)

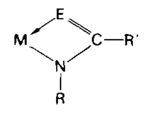


$$Me_xMCl_{5-x} + RNCO \rightarrow MCl_3(-N(R)-C(=O)-Me)_2$$

(besides other products)

(X = 1,2,3; M = Nb, Ta; R = Me, Ph)

The analogous thio derivatives have been obtained by using organic isothiocyanates.[63,64] Infrared evidence seems to indicate that the organic ligands in these compounds are probably chelated,



(E = O, S)

as for the amido complexes of rhenium previously described (3. A. (iv)). The insertion reaction of an organic isocyanate into the metal–hydrogen bond leads to the synthesis of carboxamido complexes[65,66]:

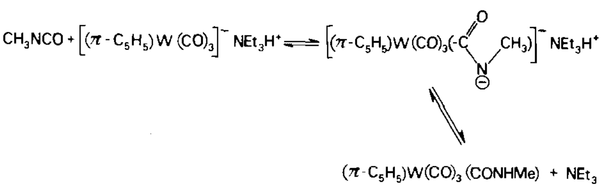
$$(\pi\text{-}C_5H_5)W(CO)_3H + MeNCO \underset{}{\overset{Et_3N}{\rightleftharpoons}} (\pi\text{-}C_5H_5)W(CO)_3(CONHMe)$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2H + Bu^tNCO \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(CONHBu^t)$$

The iron product has been isolated in very low yields. In the case of the tungsten complex and in the absence of a base like NEt_3, the reaction does not proceed. The role of the amine seems to be of generating *in situ* an ionic species:

$$(\pi\text{-}C_5H_5)W(CO)_3H + NEt_3 \rightleftharpoons [(\pi\text{-}C_5H_5)W(CO)_3]^- NEt_3H^+$$

Nucleophilic attack of the ion on the isocyanate leads to the desired product[53,65]:



D. Other Products

We have already discussed the reaction of rhenium oxo complexes with PhNCO which leads to the isolation of nitrene derivatives with carbon dioxide evolution (2. A.). Other transition metal oxo and peroxo complexes react in an analogous way, but the organometallic products have not been specified[4]. Characterized adducts between $Pt(PPh_3)_2(O_2)$ and PhNCO or PhNCS have been reported[56]. They have the stoichiometry $Pt(PPh_3)_2(O_2)\cdot 2PhNCO$ and $Pt(PPh_3)_2(O_2)\cdot PhNCS$, and possibly the organic ligand is inserted into the metal oxygen bond giving a cyclic peroxide related to those obtained by reacting $Pt(PPh_3)_2(O_2)$ with organic carbonyl derivatives[28].

The reaction of PhNCO with $Ru_3(CO)_{12}$ in benzene gives $Ru_3(CO)_{10}NPh$ in 20% yields, a derivative with a triply bridged nitrene ligand, and a trace amount of $Ru_3(CO)_9(NPh)_2$[67]. The same reaction conducted with PhNCS gives two unidentified products.

From the reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ with $ClCH_2NCO$, a product analysing as $\{(\pi\text{-}C_5H_5)Fe\}_3(CH_2NCO)$ has been isolated in low yields[68]. On the basis of its ν_{NCO} (2120 cm^{-1}) which is shifted to lower frequencies by about 150 cm^{-1} relative to ν_{NCO} in $(\pi\text{-}C_5H_5)Mo(CO)_3(CH_2NCO)$, a π-coordination of the –NCO group bridging two iron atoms has been proposed[68].

5. Syntheses of Organic Products via Transition Metal Complexes

The organic syntheses of many nitrogen containing compounds can be catalytically achieved by using metal carbonyl derivatives as catalysts[69]. When organic isocyanates as substrates and metal carbonyls as catalysts are used, high yields of the corresponding imines have been recently obtained[70]:

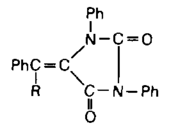
$$RCHO + R'NCO \xrightarrow{M_x(CO)_y} RCH{=}NR' + CO_2$$

(R = MeCH=CH, PhCH=CH, Ph; $M_x(CO)_y$ = $Co_2(CO)_8$, $W(CO)_6$, $Fe(CO)_5$, $Mo(CO)_6$, $Cr(CO)_6$)

With sulphonyl isocyanate ($R' = PhSO_2$) the reaction takes place smoothly; however with phenyl isocyanate (R' = Ph) longer reaction time and lower yields were observed.

Among the various catalysts employed, $Co_2(CO)_8$ was found to be the most efficient. A related catalytic reaction was observed by using aromatic nitro compounds instead of isocyanates under carbon monoxide pressure and by using metal carbonyls such as $Rh_6(CO)_{16}$, $Co_2(CO)_8$, $Fe(CO)_5$, $Ru_3(CO)_{12}$ as catalysts[71]. It is known, in fact, that aromatic nitro compounds can be transformed catalytically into the corresponding isocyanates in the presence of carbon monoxide[72]. However a mechanism involving a nitrene intermediate, which reacts directly with the aldehyde, was considered more likely[71]. The formation of a nitrene complex intermediate was also proposed in the reaction of nitrobenzene with CO and H_2 under pressure, giving aniline and 1,3-phenylurea through the catalytic action of $Ru_3(CO)_{12}$ or $Ru(CO)_5$[73].

The reactions of acetylenes with isocyanates in the presence of iron pentacarbonyl have been shown to give mainly hydantoin derivatives[74,75],



(R = H, PhC≡C)

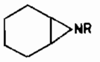
The organic isocyanates, RNCO ($R = o\text{-}CH_3\text{–}C_6H_4$, Cy) were catalytically converted in high yields into the corresponding carbodiimides by using various metal carbonyls as catalysts at high temperatures[76]. The following mechanism was proposed:

$$L_nM\text{–}C{\equiv}O + RNCO \rightarrow L_nM\text{–}CNR + CO_2$$

$$L_nM\text{–}CNR + RNCO \rightarrow L_nM\text{–}C{\equiv}O + RN{=}C{=}NR$$

The isolation of isocyanide complexes from the reaction of metal carbonyls with organic isocyanates[59,76] seems to support this reaction path.

The catalytic formation of intermediate nitrenes has been postulated during the reactions of organic azides with an organic substrate in the presence of copper and copper salts[10]. Copper and copper(I) chloride catalyse the transformation of $PhSO_2N_3$, in refluxing methanol, into the corresponding amide, besides other products[77]. When the reaction is conducted in cyclohexene solution, various products can be isolated, including the derivative of the nitrene residue inserted into the olefinic double bond,[77b]

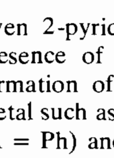


Even 2-pyridyl azide reacts with benzonitrile in the presence of copper at 120° C *via* the intermediate formation of the corresponding nitrene residue[78]. A metal such as sodium also induces the $RN–N_2$ cleavage (R = Ph) and evidence has been reported for the formation of RNNa and $RNNa_2$[79].

However complexes such as $Cu(PPh_3)_3Cl$ and $Au(PPh_3)Cl$ do not catalyze the transformation in ethanolic medium of p-$CH_3C_6H_4SO_2N_3$ into the corresponding amide. From the reaction in the presence of the copper complex, the phosphinimine adduct is isolated, while the metal is recovered as the tetrameric $[Cu(PPh_3)Cl]_4$[80].

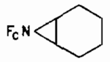
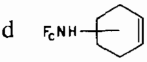
Aromatic azides and diazides are decomposed in benzene by diironnonacarbonyl to give a variety of organic products, besides some bis(tricarbonyliron) complexes already mentioned[42]. However the reaction are more complex than uncatalyzed pyrolysis of the azides, and do not provide a convenient route to the synthesis of organic products from the azides[42].

The thermolysis and photolysis of the ferrocenyl azide



(F_cN_3) in cyclohexane, cyclohexene and benzene have been studied[81].

In these reactions the basic skeleton of the ferrocene remains unchanged, while various types of reactions occur at the $–N_3$ substituent. Since the ferrocenyl azide eliminates nitrogen smoothly at 70–80° C, while aromatic azides usually decompose at 140–170° C, a participation of the metal in the formation of a nitrene intermediate was consequently suggested[81].

Thermolysis in benzene under nitrogen gave the azaferrocene, $F_cN{=}NF_c$, and aminoferrocene, F_cNH_2, besides products arising from the C–N_3 cleavage. In the presence of oxygen nitroferrocene, F_cNO_2, is the main product, suggesting the intermediacy of a triplet nitrene. In cyclohexene as the solvent the presence of oxygen does not change the amount of the two products isolated in low yields, that is  and  which lead to the hypothesis that these compounds are derived mainly from singlet nitrene[81].

6. Discussion and Conclusions

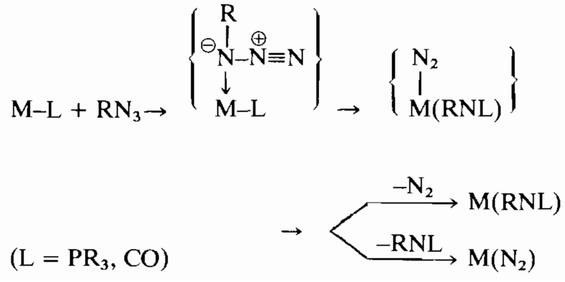
The first relevant difference between the organometallic chemistry of ligands like organic azides and isocyanates is that only the latter can behave as unchanged ligands with transition metals. Organic azides generally yield products in which at least one of the molecules involved in the reaction has lost nitrogen, as a consequence of the breaking of the $RN–N_2$ bond (in some cases the $R–N_3$ bond is also broken). This is in agreement with the general behaviour of covalent azides in organic chemistry, which is primarily determined by the weakness of the $RN–N_2$ bond and which again reflects the stability of molecular nitrogen[10]. A formal bond order of 1.5 is predicted for this bond. On the other hand the RN=CO bond of organic isocyanates is not so readily broken, and carbon monoxide is displaced only in the reactions which lead to the formation of stable derivatives of the nitrene (2. A.) and ureylene ligand (4. B.), or when the NR residue is involved in bonding with more than one metal center.

To our knowledge, only one case has been reported where the unique molecule of the azide involved in a reaction has not lost nitrogen[82]:

$$Co(PCy_3)_2Br_2 \xrightarrow[CH_2Cl_2]{RN_3/0^\circ C} Co(RN{=}N{-}N{=}PCy_3)Br_2$$

(R = 2-carbonylfuran)

The reaction conducted at room temperature gives $Co(RN{=}PCy_3)_2Br_2$. This parallels the reactions of the azides with tricovalent phosphorus derivatives without the presence of the metal[10]. This is an important result in view of the plausible mechanism of the organometallic reactions of the azides. It seems in fact to suggest that in most cases the first step of the reaction sequence involves a labile coordination of the azide, followed by its reaction with a ligand other than a phosphine previously bound to the metal with concomitant loss of nitrogen:



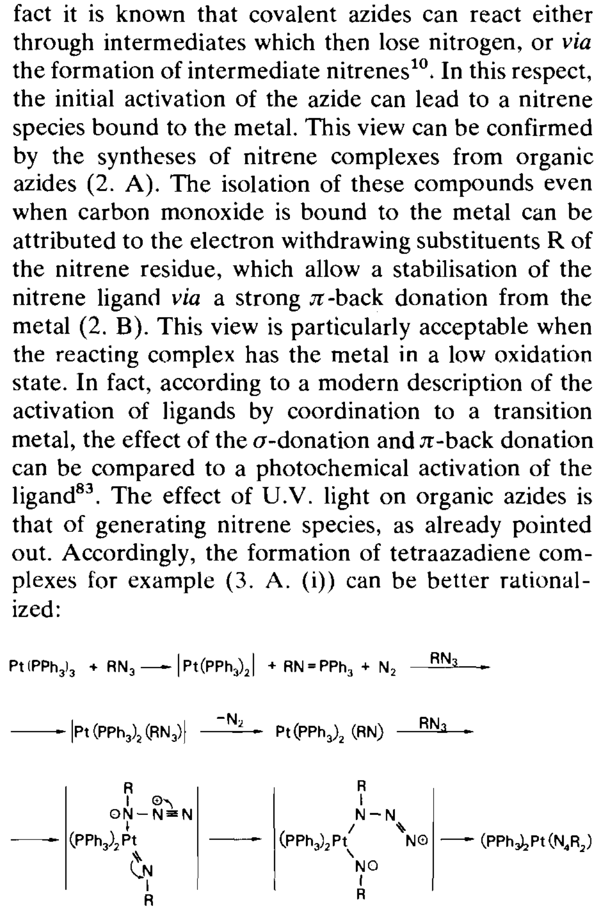
$$M{-}L + RN_3 \rightarrow \left\{\begin{matrix} R \\ {}^{\ominus}\overset{|}{N}{-}\overset{\oplus}{N}{\equiv}N \\ \downarrow \\ M{-}L \end{matrix}\right\} \rightarrow \left\{\begin{matrix} N_2 \\ | \\ M(RNL) \end{matrix}\right\}$$

$$\rightarrow \begin{cases} \xrightarrow{-N_2} M(RNL) \\ \xrightarrow{-RNL} M(N_2) \end{cases}$$

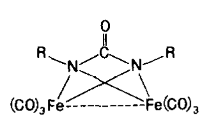
(L = PR_3, CO)

In some particular cases (L = CO; 3. B. (iii)) a dinitrogen complex is isolated instead of the isocyanate derivative.

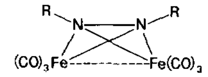
An activation of the azide by preliminary coordination to a transition metal is supported by the fact that the reaction with carbon monoxide does not occur under mild conditions and in the absence of the metal. However a description of the mechanism of these reactions poses the same problems which arise on considering the organic reaction of covalent azides. In fact it is known that covalent azides can react either through intermediates which then lose nitrogen, or *via* the formation of intermediate nitrenes[10]. In this respect, the initial activation of the azide can lead to a nitrene species bound to the metal. This view can be confirmed by the syntheses of nitrene complexes from organic azides (2. A). The isolation of these compounds even when carbon monoxide is bound to the metal can be attributed to the electron withdrawing substituents R of the nitrene residue, which allow a stabilisation of the nitrene ligand *via* a strong π-back donation from the metal (2. B). This view is particularly acceptable when the reacting complex has the metal in a low oxidation state. In fact, according to a modern description of the activation of ligands by coordination to a transition metal, the effect of the σ-donation and π-back donation can be compared to a photochemical activation of the ligand[83]. The effect of U.V. light on organic azides is that of generating nitrene species, as already pointed out. Accordingly, the formation of tetraazadiene complexes for example (3. A. (i)) can be better rationalized:



This scheme parallels the 1,3-dipolar addition reactions of organic azides and it fits with the view that the nitrogen of the nitrene ligand bound to a metal in a low oxidation state is essentially negatively charged (2. B). On considering the formation of an intermediate nitrene complex, it can also be explained why a tetraazadiene derivative is formed even when carbon monoxide is coordinated to the metal (3. A. (i)). Moreover this view is in accordance with the observation that a derivative such as



is the product of the spontaneous rearrangement of the azo complex,



which inserts carbon monoxide into the N–N bond (3. A. (iii)). This type of product suggests the intermediate formation of nitrene species[17], which are presumably also involved in the formation of amido and imino derivatives (3. A. (iv)). However, the formation of ureylene derivatives *via* the reaction of the azide with an intermediate isocyanate complex can also provide an acceptable reaction path in other cases (3. A. (iii)). The isolation of the platinum complex, $\mathrm{Pt(PPh_3)_2(RN_3\overset{\overset{O}{\|}}{C}NR)}$ seems to support this hypothesis. In any case, these considerations are not inconsistent with the formation of an intermediate nitrene complex.


$\mathrm{Pt(PPh_3)_2(RN_3\overset{\overset{O}{\|}}{C}NR)}$

When the reactions of organic isocyanates are considered, the intermediate formation of an isocyanate complex is likely. Such a complex, however, has been isolated only in a few cases (4. A). Further reaction with the ligand can lead to the ureylene derivatives (4. B), as has also been demonstrated by the reactions of organic isothiocyanates, although in this case sulphur instead of carbon monoxide abstraction is involved. The formation of other products such as carboxamido derivatives (4. C), simply follows the organic chemistry of isocyanates. Intermediate nitrene complexes seem also to be involved in the reactions of organic azides with transition metal complexes in protic solvents[31]. In this case, protonation by the solvent leads to M–NHR derivatives; if carbon monoxide is also present, an insertion of CO into the M–NHR bond can occur, leading to carboxamido complexes (3. B. (i) and 3. B. (ii)). Esther complexes such as $L_nM{-}COOR$ (3. B. (iii)) can originate from the alcoholysis of intermediate carboxamido derivatives[31,84,85], although the attack by the solvent on an unknown cationic carbonyl intermediate complex cannot be excluded[86].

Finally, in the reactions in protic solvents azido complexes are usually formed, and they probably originate from the oxidative addition reactions of RN_3 to the complex (3. B. (iii)); in fact a complex such as $Pt(PPh_3)_2(N_3)(R)$ ($R = p\text{-}CH_3C_6H_4SO_2$) has been isolated from the reaction of $Pt(PPh_3)_3$ and RN_3 in ethanol medium. When carbon monoxide is present in the starting material, M–NCO instead of M–N_3 derivatives are sometimes formed (3. B. (ii)).

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