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Conversion of Alkynes and Nitriles into Organo and Organonitrogenated Species at Group VI and VII Dinitrogen-Binding Metal Centers. Synthesis of Some Vinylidene and Alkynyl Complexes of Rhenium

M. F. N. N. Carvalho[1], R. Herrmann[2], and A. J. L. Pombeiro[1,*]

[1] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

[2] Organisch-Chemisches Institut, Technische Universität München, D-8046 Garching, Federal Republic of Germany

Summary. The reactions of phenylacetylene and other alkynes [$HC{\equiv}CCH_2OH$, $HC{\equiv}C(CH_2)_2OH$, $HC{\equiv}CCH_2CMe_2CH_2COCH_3$, $HC{\equiv}CSiMe_3$ and $MeC{\equiv}CSiMe_3$], in the presence of acetonitrile or benzonitrile, with the following complexes have been investigated usually at room temperature: *trans*-$[Mo(N_2)_2L_4]$ ($L = PMe_2Ph$), *cis*-$[Mo(N_2)_2(PMePh_2)_4]$, *cis*-$[W(N_2)_2L_4]$, *trans*-$[ReCl(N_2)L_4]$, *mer*-$[ReCl(N_2)(PPh_3)L'_3]$ $\{L' = P(OMe)_3\}$, $[ReCl_2(N_2COPh)L'_3]$ and $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NCMe)]$. Cyclic trimerization was the main reaction detected for phenylacetylene (except for the Mn complex), although dimers, products of hydrogenation and species derived from alkyne/nitrile coupling were also formed in smaller amounts; for the Mo- or W-systems, the total yields were below ca. 40% relative to the metal, but the Re-systems exhibited a modest catalytic activity. The other alkynes underwent, also in low yields, mainly dimerization, cyclic or linear trimerization, apart from, to a smaller extent, coupling reactions with the nitriles or hydrogenation. The alkynyl complexes $[ReCl(C{\equiv}CPh)\{P(O)(OMe)_2\}(PPh_3)L'_2]$ and $[ReCl(C{\equiv}CPh)\{P(O)(OMe)_2\}(NCMe)_2L']$ were prepared by reaction of *mer*-$[ReCl(N_2)(PPh_3)L'_3]$ with $PhC{\equiv}CH$, in the absence and in the presence of $NCMe$, respectively, whereas the benzonitrile/dinitrogen complex $[ReCl(N_2)(CNPh)L'_3]$ was obtained either by reaction of that N_2-complex with $NCPh$ or by the reaction of $[ReCl_2(N_2COPh)L'_3]$ with $NCPh$ in the presence of $NaOMe$. The vinylidene compound *trans*-$[Re(CNMe)(C{=}CHPh)(dppe)_2][BF_4]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) was formed by reaction of *trans*-$[ReCl(CNMe)(dppe)_2]$ with $PhC{\equiv}CH$, in the presence of $Tl[BF_4]$, which did not lead to the formation of detectable amounts of any alkyne-derived organic product.

Keywords. Alkynes; Nitriles; Dinitrogen complexes; Alkynyl complexes; Vinylidene complexes; Phosphite complexes; Phosphonate complexes.

Umsetzung von Alkinen und Nitrilen zu Organo- und Organostickstoff-Spezies an distickstoffbindende Metallzentren der VI. und VII. Gruppe. Synthese einiger Vinyliden- und Alkinyl-Komplexe des Rhenium

Zusammenfassung. Die Reaktionen von Phenylacetylen und anderen Alkinen [$HC{\equiv}CCH_2OH$, $HC{\equiv}C(CH_2)_2OH$, $HC{\equiv}CCH_2CMe_2CH_2COCH_3$, $HC{\equiv}CSiMe_3$ und $MeC{\equiv}CSiMe_3$] in Gegenwart von Acetonitril oder Benzonitril mit den folgenden Komplexen wurde wie üblich bei Raumtemperatur untersucht: *trans*-$[Mo(N_2)_2L_4]$ ($L = PMePh$), *cis*-$[Mo(N_2)_2(PMePh_2)_4]$, *cis*-$[W(N_2)_2L_4]$, *trans*-$[ReCl(N_2)L_4]$, *mer*-$[ReCl(N_2)(PPh_3)L'_3]$ $\{L' = P(OMe)_3\}$, $[ReCl_2(N_2COPh)L'_3]$ und $[(\eta^5\text{-}MeC_5H_4)\text{-}Mn(CO)_2(NCMe)]$. Die Hauptreaktion für Phenylacetylen war stets die cyclische Trimerisierung (mit Ausnahme des Mn-Komplexes), obwohl auch Hydrogenierungsprodukte und Spezies aus einer Alkin/Nitril-Kupplung in kleineren Mengen aufgefunden wurden; für die Mo- oder W-Systeme waren die Ausbeuten unter etwa 40% relativ zum Metall, die Re-Systeme zeigten eine schwache katalytische Aktivität. Die anderen Alkine gingen (auch in niedrigen Ausbeuten) hauptsächlich Dimerisierung, cyclische oder lineare Trimerisierung neben (in noch geringerem Maßstab) Kupplungsreaktionen mit den Nitrilen oder Hydrogenierung ein. Die Alkinylkomplexe $[ReCl(C{\equiv}CPh)\{P(O)(OMe)_2\}(PPh_3)L'_2]$ und $[ReCl(C{\equiv}CPh)\{P(O)(OMe)_2\}(NCMe)_2L']$ wurden aus der Reaktion von *mer*-$[ReCl(N_2)(PPh_3)L'_3]$ mit $PhC{\equiv}CH$ sowohl in Abwesenheit als auch in Gegenwart von NC*Me* gebildet, wohingegen der Benzonitril/Distickstoff-Komplex $[ReCl(N_2)(NCPh)L'_3]$ entweder aus der Reaktion dieses N_2-Komplexes mit NC*Ph* oder über die Reaktion von $[ReCl_2(N_2COPh)L'_3]$ mit NC*Ph* in Gegenwart von NaO*Me* gebildet wurde. Die Vinylidenverbindung *trans*-[Re(CN*Me*)(*C*=CH*Ph*)(*dppe*)$_2$] $[BF_4]$ (*dppe* = $Ph_2PCH_2CH_2PPh_2$) wurde in der Reaktion von *trans*-[ReCl(CN*Me*)-(*dppe*)$_2$] mit $PhC{\equiv}CH$ in der Gegenwart von $Tl[BF_4]$ gebildet, wobei keine detektierbaren Mengen irgendeines von Alkin abgeleiteten organischen Produkts entstanden.

Introduction

In spite of their potential application in catalysis in view of the common lability of the dinitrogen ligands towards facile displacement, N_2-complexes have not yet been explored for that purpose, except in a limited number of cases [1], commonly involving hydrogenation, isomerization or polimerization of olefins [2], although very rare examples of catalytic activation of alkynes have been reported [3, 4].

Following our interest in the activation of unsaturated substrates by nitrogenase [5], we have been investigating the reactions of alkynes and isocyanides at dinitrogen-binding metal centers and observed in occurrence of H-migration reactions along the C-framework of the alkyne at the $\{ReCl(dppe)_2\}$ (*dppe* = $Ph_2PCH_2CH_2PPh_2$) metal site, to give the vinylidene or the phenylallene complexes *trans*-[ReCl(=C=CHR)(*dppe*)$_2$] (R = alkyl or aryl) [6] or *trans*-[ReCl(η^2–$\overline{CH_2}$–$\overline{C{=}CHPh}$)(*dppe*)$_2$] [7] from the reactions of *trans*-$[ReCl(N_2)(dppe)_2]$ with 1-alkynes ($RC{\equiv}CH$) or 1-phenyl-1-propyne ($CH_3C{\equiv}CPh$), respectively. The related centers $\{M(dppe)_2\}$ (M = Mo or W) undergo C–H oxidative addition by reaction of $RC{\equiv}CH$ with *trans*-$[M(N_2)_2(dppe)_2]$ to give alkynyl or alkynyl-hydrido complexes, namely *trans*-$[M(C{\equiv}CR)_2(dppe)_2]$ and $[MH_2(C{\equiv}CR)_2(dppe)_2]$ [8], in agreement with the greater lability of the two N_2 ligands and easier oxidation of these Mo or W species as compared with the abovementioned Re–N_2 complex.

The products of these reactions are susceptible to protonation to give a variety of carbyne or carbene complexes [8, 9]. However, no metal-free organic derivative of the alkyne appears to be formed in such reactions, which proceed in the coordination sphere of the metal centers with the two robust chelating *dppe* ligands.

Therefore, we have initiated the study of the activation of alkynes by N_2-complexes with labile co-ligands, and reported [4] that $[CoH(N_2)(PPh_3)_3]$ catalyses their oligomerization and cyclization reactions under mild conditions. A cocyclization reaction of phenylacetylene with acetonitrile was also claimed [4] to give (although in low yields) 4,6-dimethyl-5-phenyl-pyrimidine, but our results indicate that such a product does not appear to be formed.

In the present study we extend pertient investigations to a variety of group VI and VII transition-metal centers, which can also bind dinitrogen and generally present other labile co-ligands.

Results and Discussion

Organic Derivatives

The reactions of the alkynes with selected complexes with N_2-binding metal sites were performed in the presence of a nitrile, commonly acetonitrile (CH_3CN), although in a few cases benzonitrile (*Ph*CN) (and in one case, cyanamide, $NCNH_2$) have been used. They were usually performed under mild conditions (room temperature) but in a few cases, reflux or irradiation was used.

For comparison, the reactivity of a common substrate (phenylacetylene in acetonitrile) was studied with each of the following complexes: *trans*-$[Mo(N_2)_2(PMe_2Ph)_4]$, *cis*-$[Mo(N_2)_2(PMePh_2)_4]$, *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, *mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$, $[ReCl_2(N_2COPh)\{P(OMe)_3\}_3]$, and $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NCMe)]$. The organic products identified by GC–MS analyses are listed in Table 1.

Cyclic trimers of phenylacetylene (usually two or three isomers) were generally found to be the main products of the reactions, with the exception of the manganese complex for which they were not detected. Although particularly for the Mo- and W-dinitrogen complexes the yields were low (below ca. 40% relative to the metal), the Re systems, mainly the benzoyldiazenido complex $[ReCl_2(N_2COPh)\{P(OMe)_3\}_3]$, exhibited, although modestly, some catalytic activity. This compound is a known precursor for rhenium-dinitrogen complexes formed by reductive elimination of benzoyl chloride in the presence of a suitable substrate, and such complexes may also be involved in these reactions.

Other organic products formed, although in considerably lower yields than the cyclic trimers, are mainly dimers of phenylacetylene and products of their hydrogenation, apart from different species derived from coupling of acetonitrile to this alkyne (1:1 or 1:2 addition products such as pyridine derivatives).

With *cis*-$[Mo(N_2)_2(PMePh_2)_4]$, hydrolysis of the alkyne occurs to some extent.

Therefore, a clean reaction only occurred with *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, where cyclic trimers of the alkyne were the only detected products, while a variety of species was formed, in low selectivity, with the other metal complexes.

The cymantrene derivative containing the N_2-binding metal site $\{(\eta^5\text{-}MeC_5H_4)\text{-}Mn(CO)_2\}$ with the smallest number of labile ligands, does not react at all under the mild standard conditions, but only on irradiation with UV light; hydrogenation of phenylacetylene and partial coupling with acetonitrile were found in this case.

Comparing these results with those previously obtained [4] for the dinitrogen complex $[CoH(N_2)(PPh_3)_3]$, it appears that, with the exception of the Mn complex,

Table 1. Organic products from the reactions of phenylacetylene with complex **M** in acetonitrile at room temperature

M	Organic products[a]	
trans-$[Mo(N_2)_2(PMe_2Ph)_4]$[b]	Cyclic trimers (2 isomers 1:1)	(5%)
	Dimers	(<1%)
	Hydrogenated dimers	(<1%)
	Addition products:	
	*Ph*CCH + CH_3CN (2 isomers 1:1)[h]	(3%)
	2-Substituted pyridine (2 isomers)	(2.5%)
cis-$[Mo(N_2)_2(PMePh_2)_4]$[c]	Cyclic trimers (2 isomers)	(5%)
	Dimers	(3%)
	Hydrogenated dimers	(2%)
	Hydrolysis product [from *Ph*CCH + H_2O (1:2)]:	
	$HOCH(Ph)CH_2OH$	(3%)
cis-$[W(N_2)_2(PMe_2Ph)_4]$[c]	Cyclic trimers (3 isomers 1:1:1)	(5%)
	Hydrogenated dimers	(1%)
	Addition products:	
	*Ph*C≡C–C≡N	(2%)
	2-Substituted pyridine	(<1%)
trans-$[ReCl(N_2)(PMe_2Ph)_4]$[d]	Cyclic trimers	(10%)
mer-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$[d,e]	Cyclic trimers	(10%)
	Dimers (2 isomers 1:1)	(3%)
	Hydrogenated dimer	(2%)
	*Ph*CH=CH_2	(1%)
	PhCH_2CH_3	(<1%)
$[ReCl_2(N_2COPh)\{P(OMe)_3\}_3]$[b,f]	Cyclic trimers (3 isomers)	(30%)
	Linear trimer	(5%)
	Hydrogenated dimer	(2%)
	Addition product:	
	2-Substituted pyridine	(3%)
$[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NCMe)]$[c,g]	Addition product:	
	*Ph*C≡CH + CH_3CN (1:1)[h]	(5%)
	*Ph*CH=CH_2	(10%)
	PhCH_2CH_3	(2%)
	Ph$COCH_3$	(5%)

[a] Approximate molar yields in brackets, relative to unreacted *Ph*CCH (ca. tenfold molar excess relative to the metal)

[b] 20 hours

[c] 5 days

[d] 1 day

[e] *Ph*COO*Et*, $Et_2P(O)(OMe)$ and $PHCH_2CN$ are also obtained if the reaction occurs in the presence of a mixture of CH_3CN/Et_2O (1:1) as a solvent

[f] With added *Me*OH, upon reflux, *Ph*$COCH_3$, Ph_2CO and PHCOO*Me* are also obtained

[g] Irradiation with a high pressure uv lamp using *Me*OH as solvent, (no reaction was observed in CH_3CN at the conditions used for the other reactions)

[h] Unambigous formulation not established

Table 2. Organic products obtained from the reactions of different alkynes $RC{\equiv}CR'(L)$ with complexes **M**[a]

M	$RC{\equiv}CR'(L)$			
	R H *R'* CH_2OH	H $(CH_2)_2OH$	H $CH_2CMe_2CH_2COCH_3$	H[b] $SiMe_3$	*Me* $SiMe_3$
trans-$[Mo(N_2)_2(PMe_2Ph)_4]$		$L+H_2O$ (1%) $L+CH_3CN(1:1)$ (1%) 2-Substituted pyridine (<1%) $C_6H_5(CH_2)_2OH$ (3%)		2-Substituted pyridine (3 isomers) (<1%) $L+CH_3CN(1:1)$ (3.5%) Cyclic trimers (10%)	
cis-$[Mo(N_2)_2(PMePh_2)_4]$				Dimer (5%) Hydrogenated dimer (3.5%) 1-Substituted trimer (1%) Trimer (1%)	
mer-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$				Hydrolysed trimer (8%) $NCCH(SiMe_3)_2$ (3%)	
$[ReCl_2(N_2COPh)\{P(OMe)_3\}_3]$[c]	$PhCOCCCH_2OH$ (2%) $PhCH_2CH_3$ (1%) $PhCH{=}CH_2$ (1%) PhCOOMe (12%) Ph_2CO (3%)		Hydrogenated dimer (3%) $CH_3CONHCH_3$ (10%) $PhCOCH_2OCH_3$ (3%) Addition product[d] (2%)	$PhCOCH{=}C{=}CH_2$ (1%) $Me_3SiC(Cl){=}CHCl$ (<1%) $PhCOCH_2CH_3$ (1%) $PhCOOMe$ (10%) Ph_2CO (8%) $Me_3SiC{\equiv}CSiMe_3$ (1%) $Me_3Si(CH_2)_4SiMe_3$ (1%)	Dimethyl pyridine (1%) $PhCOOMe$ (15%) Addition product[e] (1%)

[a] In acetonitrile at room temperature unless stated otherwise; approximate molar yields (in brackets) relative to unreacted alkyne

[b] In CH_2Cl_2

[c] On reflux with added *Me*OH

[d] Formulated as $CH_3CH{=}CHCH_2CMe_2CH_2COCH_3$ or a cyclic isomer

[e] Formulated as $PhCOC(CH_3){=}C(CHCH_3CH_2OH)\,SiMe_3$

which is not directly comparable, the ability of those metal centers towards the overall activation of phenylacetylene increases from group VI to group VIII metal sites.

Although phenylacetylene was studied in a more systematic way, other alkynes (either terminal or internal ones) were also investigated, in particular $HC{\equiv}CCH_2OH$, $HC{\equiv}C(CH_2)_2OH$, $HC{\equiv}CCH_2CMe_2CH_2COCH_3$, $Me_3SiC{\equiv}CH$ or $Me_3SiC{\equiv}CCH_3$, and the results are presented in Table 2.

Oligomerization is the main reaction path with the silylated alkynes, leading to linear products with *cis*-$[Mo(N_2)_2(PMePh_2)_4]$ and *mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$ and to cyclic products with *trans*-$[Mo(N_2)(PMe_2Ph)_4]$. The latter complex also led to the formation of small amounts of coupling products of acetonitrile not only with the silylated alkynes, but also with $HC{\equiv}C(CH_2)_2OH$. In the case of the diazenido complex $[ReCl_2(N_2COPh)\{P(OMe)_3\}_3]$, addition products of $MeC{\equiv}CSiMe_3$ were detected in very low yields, whereas $HC{\equiv}CCH_2CMe_2CH_2COMe$ underwent hydrogenation/dimerization. Attempts to increase the reactivity of this complex by promoting the formation of a possible intermediate dinitrogen complex by means of addition of methanol under reflux gave, with all alkynes studied, mainly the expected derivatives of the benzoyl group, such as methyl benzoate, but no improvement in the yields of organic products derived from the alkynes.

The selectivity of the reaction usually is increased considerably if benzonitrile is used instead of acetonitrile. Generally, only one or two organic products could be detected; benzyl cyanide was formed in all cases, from alkyne/nitrile coupling and hydrolysis. The results are included in Table 3.

Apart from the abovementioned manganese complex, other compounds with a robust N_2-binding metal site have also been tested, in particular *trans*-$[ReCl(N_2)(dppe)_2]$ and *trans*-$[ReCl(CNMe)(dppe)_2]$. However, in contrast with the other complexes indicated above, no alkyne-derived organic product was detected in the reaction solution, but stable organometallic complexes with vinylidene ligands have been formed. The already reported [6] complexes *trans*-$[ReCl(=C=CHR)(dppe)_2]$ are known to be derived from the parent dinitrogen complex. As products of the

Table 3. Organic products from the reaction of phenylacetylene with complexes **M** in benzonitrile[a]

M					
cis-$[W(N_2)_2(PMe_2Ph)_4]$[b]		*mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$[c]		$[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(NCMe)]$[d,e]	
$PhCH_2CN$[f]	(25%)	$PhCH_2CN$[f]	(20%)	$PhCH_2CN$[f]	(30%)
Addition product: (nitrile/alkyne 3:1)[g]	(2%)	$PhCH_2CH_3$	(2%)		

[a] At room temperature, approximate yields in brackets relative to unreacted $PhC{\equiv}CH$

[b] Reaction time 5 days

[c] Reaction time 1 hour; in the presence of $NCNH_2$, $PhCH{=}CH_2$ (> 50%) and alkyne trimers (2%) are formed

[d] Irradiation with a 300 W W-filament lamp during 10 hours

[e] In the presence of $NCNH_2$ and using Et_2O as solvent, $PhCH{=}CH_2$ (2%) and toluene (30%) are formed

[f] Possibly derived from 1:1 alkyne/nitrile coupling and hydrolysis

[g] $PhC{\equiv}C{-}N{=}C(Ph)C(H){=}NCHPhC{\equiv}N$ or $Ph{-}C{\equiv}C{-}N{=}C(Ph)C(Ph){=}NCH_2C{\equiv}N$

reaction of the isocyanide complex with *Ph*C≡CH novel alkynyl complexes have been isolated from the reaction of this alkyne with *mer*-[ReCl(N_2)(PPh_3){$P(OMe)_3$}$_3$]. However, it has not yet been ascertained if complexes of these types are intermediates in the production of the organic products.

Organometallic Complexes

The coordinating abilities of alkynes and nitriles to transition metal centers have been well recognized and a wide variety of complexes has been reported [7]. For our systems, in view of the common low yields of the organic products, stable coordination compounds of those substrates (or derived ligands) were also expected and have indeed been isolated (Tables 3 and 4).

Substitution of the chloride in *trans* position to the isocyanide at *trans*-[ReCl(CN*Me*)(*dppe*)$_2$] provides a convenient method for the syntheses of complexes of the general formula *trans*-[Re*L*(CN*Me*)(*dppe*)$_2$]$^+$ (*L* = NC*Me* or CNR where *R* = alkyl or aryl) [10].

Following this route, the green/red dichromatic vinylidene species *trans*-[Re(CN*Me*)(C=CH*Ph*)(*dppe*)$_2$][BF_4] was formed from the reaction of the isocyanide complex with phenylacetylene in the presence of Tl[BF_4] (Eq. 1).

$$\textit{trans}\text{-[ReCl(CN}Me)(dppe)_2] + Ph\text{C}{\equiv}\text{CH} + \text{Tl[BF}_4] \longrightarrow \textit{trans}\text{-[Re(CN}Me)(\text{C}{=}\text{CH}Ph)(dppe)_2][\text{BF}_4] + \text{TlCl} \quad (1)$$

The vinylidene ligand was generated by 1,2-hydrogen migration at *Ph*C≡CH activated by the metal center, as known [6] to occur in the formation of *trans*-[ReCl(C=CH*Ph*)(*dppe*)$_2$] (*R* = alkyl or aryl) from the reactions of 1-alkynes with *trans*-[ReCl(N_2)(*dppe*)$_2$]. The presence of a ligating vinylidene is indicated by the

Table 4. Physical data for the rhenium complexes formed in the reactions (1)–(5)

Complex	Colour	Analysis (found (calcd.))% C	N	H	IR (cm^{-1})[a] ν(C≡N) or ν(N≡C)	ν(C≡C)
trans-[Re(CN*Me*)(C=CH*Ph*)(*dppe*)$_2$][BF_4][b]	green	55.8 (55.6)	1.0 (1.1)	5.2 (4.4)	2158 s	1586 s 1565 m
[ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(P*Ph*$_3$){P(O*Me*)$_3$}$_2$][c]	yellow	42.7 (42.7)		4.5 (4.6)		2015 m
[ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(NC*Me*)$_2${P(O*Me*)$_3$}]	brown	32.2 (32.0)	4.5 (4.4)	4.5 (4.1)	2250 w	2040 s
[ReCl(N_2)(NC*Ph*){P(O*Me*)$_3$}$_3$][d,e]	brown	29.0 (26.5)	3.9 (5.8)	3.9 (4.4)	2210 m	

[a] In KBr pellets
[b] With 2 CH_2Cl_2 of crystallization
[c] With 1/4 CH_2Cl_2 of crystallization
[d] No reliable elemental analysis was obtained due to decomposition
[e] ν(NN) = 2060 cm^{-1} (m)

characteristic quintet resonance pattern assigned to C=C*H*Ph, observed in the ^{1}H NMR spectrum (CD_2Cl_2) at δ 2.05 ppm ($^4J_{PH} = 3.4$ Hz); moreover, the IR spectrum shows ν(C=C) at ca. 1590–1570 cm^{-1}, whereas ν(C≡N) of the isocyanide ligand occurs at 2158 cm^{-1}.

The reaction of *Ph*C≡CH with *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)$_3$}$_3$] proceeds via quite a different route to give the alkynyl-phosphonato complex [ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(P*Ph*$_3$){P(O*Me*)$_3$}$_2$] (Eq. 2). In the IR spectrum, the observed medium intensity band at 2015 cm^{-1} is assigned to ν(C≡C) of the alkynyl ligand.

Evidence for the phosphonate ligand is provided by both IR and NMR data. IR band at 1235 cm^{-1} is assigned to ν(P=O), and the ^{1}H NMR spectrum (in $CDCl_3$) exhibits a pair of doublets (δ 3.84 and 3.75 ppm; $^3J_{(PH)} = 10.2$ Hz) which are attributed to the methyl groups of the phosphonato ligand, in agreement with similar data quoted [11], e.g., for [ReOCl$_2${P(O)(O*Me*)$_2$}(P*Ph*$_3$)], where the phosphonate ligand was possibly generated through a Michaelis–Arbuzov type rearrangement of ligating P(O*Me*)$_3$ in an ionic process involving a nucleophilic attack of liberated chloride from the parent complex [ReOCl$_3$(P*Ph*$_3$)$_2$] in refluxing *Me*OH. However, in the present study the conversion of the phosphite into the phosphonate ligand occurs under milder conditions (at room temperature) and the mechanism is still unknown.

$$\textit{mer}\text{-}[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3] + PhC{\equiv}CH \longrightarrow [ReCl(C{\equiv}CPh)\{P(O)(OMe)_2\}(PPh_3)\{P(OMe)_3\}_2] + N_2 + CH_4 \quad (2)$$

When the reaction of *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)$_3$}$_3$] with phenylacetylene is carried out in the presence of acetonitrile, further partial replacement of the neutral phosphorus ligands occurs to give [ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(NC*Me*)$_2$ {P(O*Me*)$_3$}] (Eq. 3). In the IR spectrum, the bands observed at 2250 (w), 2040 (s), and 1250 (w) cm^{-1} are assigned to ν(N≡C), ν(C≡C), and ν(P=O) of the nitrile, alkynyl and phosphonate ligands, respectively. In the ^{1}H NMR spectrum, the methyl proton resonance of the phosphonate ligand appears as a doublet [$^3J_{(PH)} = 10.7$ Hz] at $\delta = 3.63$ ppm.

$$\textit{mer}\text{-}[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3] + 2NCMe + PhC{\equiv}CH \longrightarrow [ReCl(C{\equiv}CPh)\{P(O)(OMe)_2\}(NCMe)_2\{P(OMe)_3\}] + N_2 + PPh_3 + P(OMe)_3 + CH_4 \quad (3)$$

In the absence of the alkyne, the reaction of benzonitrile with *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)$_3$}$_3$] only involves a simple replacement of the phosphine ligand to afford [ReCl(N$_2$)(NC*Ph*){P(O*Me*)$_3$}$_3$] (Eq. 4), suggesting an active role of the alkyne in the phosphite to phosphonate conversion. Substitution of P*Ph*$_3$, rather than N$_2$, by isocyanides at the parent dinitrogen complex has already been reported [12].

$$\textit{mer}\text{-}[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3] + NCPh \longrightarrow [ReCl(N_2)(NCPh)\{P(OMe)_3\}_3] + PPh_3 \quad (4)$$

[ReCl(N$_2$)(NC*Ph*){P(O*Me*)$_3$}$_3$] was also obtained in the reaction of benzonitrile with [ReCl$_2$(N$_2$CO*Ph*){P(O*Me*)$_3$}$_3$] in the presence of NaO*Me* (Eq. 5), with liberation of methylbenzoate derived from the nucleophilic attack of methoxide to

Table 5. ^{1}H NMR data[a] for the rhenium complexes formed in the reactions (1)–(5)

Complex	δ(ppm)	Integration	Assignment
trans-[Re(CN*Me*)(C=CH*Ph*)(*dppe*)$_2$][BF_4][b,c]	7.99 t[d]	1(1)	$CCHC_6H_5$ (*p*-H)
	7.4–6.4 m	42(40+2)	C_6H_5 (dppe)+$CCHC_6H_5$ (*m*-H)
	6.52 d[e]	2(2)	$CCHC_6H_5$ (*o*-H)
	2.6–2.5 m	10(8+3)	CH_2 (*dppe*)+$CNCH_3$
	2.05 q[f]	1(1)	$CCHC_6H_5$
[ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(P*Ph*$_3$){P(O*Me*)$_3$}$_2$]	7.9–7.1 m	20(15+5)	C_6H_5 (P*Ph*$_3$ + C≡C*Ph*)
	3.84 d[g]	3(3)	$P(O)(OCH_3)_2$
	3.75 d[g]	3(3)	$P(O)(OCH_3)_2$
	3.7–3.4 m	18(18)	$P(OCH_3)_3$
[ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(NC*Me*)$_2$P(O*Me*)$_3$}][c]	7.8 t[h]	1(1)	CCC_6H_5 (*p*-H)
	7.69 t[h]	2(2)	CCC_6H_5 (*m*-H)
	7.52 d[h]	2(2)	CCC_6H_5 (*o*-H)
	3.94 s	3(3)	$NCCH_3$
	3.8–3.7 m	9(9)	$P(OCH_3)_3$
	3.63 d[i]	6(6)	$P(O)(OCH_3)_2$
	3.34 s	3(3)	$NCCH_3$
[ReCl(N$_2$)(NC*Ph*){P(O*Me*)$_3$}$_3$]	7.7–7.5 m	5(5)	NCC_6H_5
	3.7–3.5 m	27(27)	$P(OCH_3)_3$

[a] In $CDCl_3$ unless stated otherwise; [b] In CD_2Cl_2
[c] Singlet [δ = 105.9 ppm rel. to P(O*Me*)$_3$] in the ^{31}P NMR spectrum
[d] $^3J_{HH}$ = 6.3 Hz; [e] $^3J_{HH}$ = 7.6 Hz; [f] $^4J_{PH}$ = 3.4 Hz; [g] $^3J_{PH}$ = 10.2 Hz; [h] $^3J_{HH}$ = 8.0 Hz; [i] $^3J_{PH}$ = 10.7 Hz

the benzoyldiazenido ligand. In its IR spectrum, $\nu(N_2)$ and $\nu(N{\equiv}C)$ are observed as medium intensity bands at 2060 and 2210 cm^{-1}, respectively.

$$[ReCl_2(N_2CO\mathit{Ph})\{P(O\mathit{Me})_3\}_3] + NC\mathit{Ph} + NaO\mathit{Me} \xrightarrow{CH_2Cl_2} [ReCl(N_2)(NC\mathit{Ph})\{P(O\mathit{Me})_3\}_3] + \mathit{Ph}COO\mathit{Me} + NaCl \quad (5)$$

Final Comments

Although the detailed mechanisms of the reported reactions are unknown, one can point out that the variety of organic products obtained from alkynes and nitriles indicates the existence of various activation and reaction mechanisms at the dinitrogen binding centers studied. However, low yields and a low selectivity are observed in most cases, although for a few systems a catalytic activity was recognized. For practical applications, optimization of the reaction conditions would be necessary. Moreover, stable organometallic complexes with nitrile or alkyne-derived vinylidene or alkynyl ligands have been isolated under suitable experimental conditions and for adequate metal sites, but their role as intermediates in the formation of the final organic products has still to be clarified.

Experimental Part

All the reactions were carried out under nitrogen, using solvents distilled and purified by standard methods. Phenylacetylene was distilled before use. All the other alkynes were used as purchased

(Aldrich) without further purification. *trans*-[ReCl(CN*Me*)(*dppe*)$_2$] [13], *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)$_3$}$_3$] [14], [ReCl$_2$(N$_2$CO*Ph*){P(O*Me*)$_3$}$_3$] [15], *trans*-[ReCl(N$_2$)(P*Me*$_2$*Ph*)$_4$] [16], *trans*-[Mo(N$_2$)$_2$(P*Me*$_2$*Ph*)$_4$] [17], *cis*-[Mo(N$_2$)$_2$(P*MePh*$_2$)$_4$] [17], *cis*-[W(N$_2$)$_2$(P*Me*$_2$*Ph*)$_4$] [18], and [(η^5-*Me*C$_5$H$_4$)Mn(CO)$_2$(NC*Me*)] [19] were prepared by published methods.

GC/MS experiments were performed in a Carlo Erba 4160 chromatograph equiped with a Crompack SIL 5 column, and a Varian Mat 1125 apparatus. ^{1}H NMR spectra were recorded with a Jeol JNM PM 60 or a Bruker CPX 300 spectrometer.

All the attempted catalytic reactions were carried out under identical conditions, although during different reactions times. Details are given for one of the cases as a typical example. The results obtained are reported in Tables 1 and 2.

To a suspension of *trans*-[ReCl(N$_2$)(P*Me*$_2$*Ph*)$_4$] (100 mg, 0.125 mmol) in acetonitrile (10 cm^3), phenylacetylene (0.2 cm^3, 1.9 mmol) was added and the mixture stirred for one day. The dark brown suspension was filtered off through a silica-gel (0.2–0.5 mesh) packed column of ca. 10 cm height. The effluent (eluted with *n*-pentane) was concentrated under vacuum and analysed by GC-MS.

In a few cases benzonitrile was used instead of acetonitrile. These results are reported in Table 3.

The organometallic species were obtained by the following procedures.

trans-[Re(CN*Me*)(C=CH*Ph*)(*dppe*)$_2$][BF$_4$]

Tl[BF$_4$] (80 mg, 0.27 mmol) was added to a solution of *trans*-[ReCl(CN*Me*)(*dppe*)$_2$] (0.25 g, 0.24 mmol) in CH_2Cl_2 (30 cm^3), and the system was stirred for 1 h. Phenylacetylene (0.1 cm^3, 0.95 mmol) was then added and the suspension refluxed for 4 h. The white solid (TlCl) was filtered off and Et_2O (22 cm^3) was added dropwise to the greenish solution until the product precipitated as a microcrystaline green solid (40% yield).

[ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(P*Ph*$_3$){P(O*Me*)$_3$}$_2$]

This complex was obtained from the reaction of *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)$_3$}$_3$] (0.20 g, 0.23 mmol) with *Ph*C≡CH (0.125 cm^3, 1.19 mmol) in CH_2Cl_2 (20 cm^3), carried out for four days at room temperature. Complete evaporation of the solvent and washing of the residue with Et_2O followed by recrystallization of the remaining brown solid from *THF*/Et_2O afforded the product as an yellow solid (ca. 20% yield).

[ReCl(C≡C*Ph*){P(O)(O*Me*)$_2$}(NC*Me*)$_2${P(O*Me*)$_3$}]

This compound was obtained by stirring a solution of *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)}$_3$}$_3$] (0.21 g, 0.24 mmol) in CH_3CN (30 cm^3) in the presence of *Ph*CCH (0.02 cm^3, 0.24 mmol), during 16 h. Evaporation of the solvent and washing of the residue with ether followed by recrystallization from CH_3CN gave the product as a brown unstable solid which was filtered off and washed with Et_2O (ca. 20% yield).

[ReCl(N$_2$)(NC*Ph*){P(O*Me*)$_3$}$_3$]

This species was obtained by refluxing a solution of [ReCl$_2$(N$_2$CO*Ph*){P(O*Me*)$_3$}$_3$] (0.20 g, 0.26 mmol) in CH_2Cl_2 (25 cm^3) with *Ph*CN (0.35 cm^3, 0.24 mmol) in the presence of NaO*Me* (0.25 g, 0.47 mmol), for 2 h. Evaporation of the solvent and washing of the residue with diethyl ether followed by recrystallization from *THF*/diethyl ether gave a brown precipitate (ca. 20% yield). This complex can also be obtained by replacement of phosphine by NC*Ph* (ca. tenfold molar excess) at *mer*-[ReCl(N$_2$)(P*Ph*$_3$){P(O*Me*)$_3$}$_3$] in *THF*.

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