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DIAZENIDO, DINITROGEN AND TRIISOCYANIDE COMPLEXES OF RHENIUM(I) WITH PHOSPHITE OR PHOSPHONITE CO-LIGANDS

M. FERNANDA, N. N. CARVALHO and ARMANDO J. L. POMBEIRO*

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais,
1096 Lisboa Codex, Portugal

Abstract—Treatment of $[\overline{\mathrm{ReCl_2(NNCO}}\mathrm{Ph)(PPh_3)_2}]$ with $P(OMe)_3$, $PPh(OEt)_2$ or $PPh(OMe)_2$, in benzene and in the presence of hot methanol, leads to the formation of $[ReCl(N_2)(PPh_3)L_3]$ [L = $P(OMe)_3$ or $PPh(OEt)_2$] or $[ReCl(N_2)\{PPh(OMe)_2\}_4]$, whereas, without hot methanol, intermediate benzoyldiazenido species are obtained. The dinitrogen complexes react with isocyanides to afford $[ReCl(CNR)_3L_2]$ [R = Me, L = $PPh(OMe)_2$; R = C_6H_4Me-$\underline{4}$, L = $P(OMe)_3$].

In contrast with the well-documented chemistry of rhenium phosphine complexes, that of phosphite or phosphonite compounds of this metal is relatively underdeveloped and, therefore, is explored in this study.

The chelating benzoyldiazenido complex, $[\overline{\mathrm{ReCl_2(NNCO}}\mathrm{Ph)(PPh_3)_2}]$, is a known suitable starting material for dinitrogen and benzoyldiazenido complexes of rhenium, commonly with phosphines as co-ligands, such as *trans*-$[ReCl(N_2)L_4]$ [L = PR_3 or $P(OMe)_3$],[1] *mer*-$[Re(\eta^2\text{-}S_2PPh_2)(N_2)(PMe_2Ph)_3]$[2] or $[ReCl_2(NNCOPh)L_3]$,[1–4] from which mono- and diisocyanide complexes, particularly *trans*-$[ReCl(CNR)L_4]$,[5] $[ReCl(N_2)(CNR)L_3]$ or $[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNR)_2(PMe_2Ph)_2]$,[6] are derived.

We extend now these studies to novel phosphite or phosphonite complexes with dinitrogen, diazenido or isocyanide ligands.

RESULTS AND DISCUSSION

$[\overline{\mathrm{ReCl_2(NNCO}}\mathrm{Ph)(PPh_3)_2}]$ reacts with a phosphite, $P(OMe)_3$, or a phosphonite, $PPh(OEt)_2$ or $PPh(OMe)_2$, in refluxing benzene, followed by addition of hot methanol, to give the dinitrogen complexes $[ReCl(N_2)(PPh_3)L_3]$ [L = $P(OMe)_3$ or $PPh(OEt)_2$] or $[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (eqs (1) and (2), Scheme 1), isolated as yellow or light brown solids.

However, if the use of hot methanol is avoided, intermediate benzoyldiazenido complexes may be isolated, such as $[ReCl_2(NNCOPh)(PPh_3)_2\{PPh(OMe)_2\}]$ obtained from the reaction of that chelate with $PPh(OMe)_2$. These complexes can undergo NN—C bond cleavage upon nucleophilic attack by methanol, with heating, to give the final dinitrogen compounds, a step which is also involved in the above mentioned and more convenient single-pot synthesis of the dinitrogen complexes.

The IR spectra of the dinitrogen compounds exhibit $\nu(N_2)$ at values (2010–1985 cm^{-1} range) which, by comparison with those known for related compounds, appear to indicate that a phosphonite behaves as a considerably stronger net electron-donor than a related phosphite ligand.

In those complexes, the N_2 and the Cl ligands are believed to be *trans* to each other, thus corresponding to an arrangement which favours the stabilization of the Re—N_2 bond.

They react with isocyanides (added in excess), in THF and at room temperature, to give the triisocyanide complexes $[ReCl(CNR)_3L_2]$ {R = C_6H_4Me-$\underline{4}$, L = $P(OMe)_3$ [eq. (3)]; R = Me, L = $PPh(OMe)_2$ [eq. (4)]}, isolated as reddish-brown or brown solids, possibly formed via intermediate mixed dinitrogen–isocyanide compounds of known types,[6] where the Re—N_2 bond (which is usually quite strong in neutral Re^I—N_2 complexes)[5] is labilized by the strong π-electron withdrawing ability of the CNR co-ligand.

Hence, the convenient application of dinitrogen compounds of rhenium to the syntheses of low-valent mono- and diisocyanide complexes with this metal has been extended to triisocyanide species.

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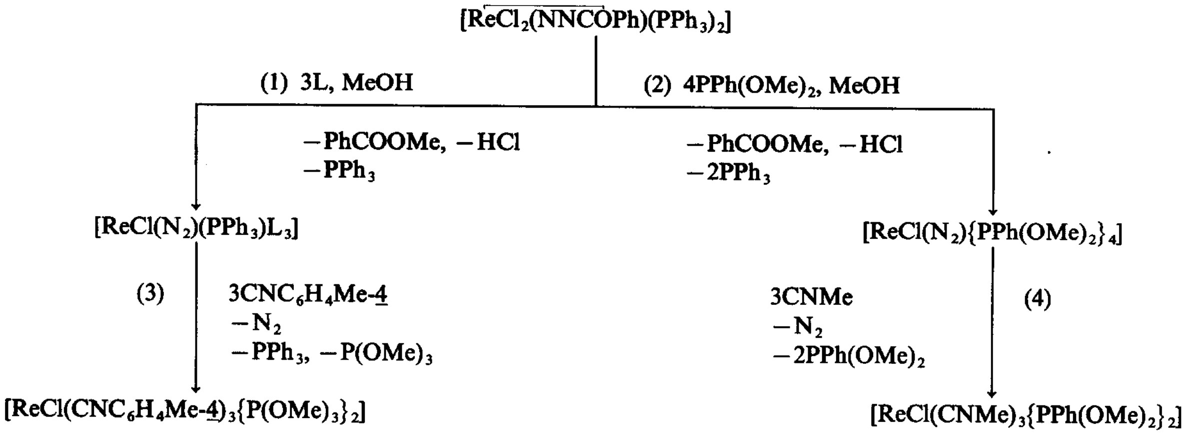
* Author to whom correspondence should be addressed.



Scheme 1. Syntheses of low-valent dinitrogen and derived triisocyanide complexes of rhenium(I) with phosphites or phosphonites as co-ligands. [Equation (1)—L = $P(OMe)_3$ or $PPh(OEt)_2$. Equation (3)—L = $P(OMe)_3$].

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