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Study on the Reactions of the Dinitrogen Complexes *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W) with Ethyldiazoacetate: Formation of an Azo Compound and of a Phosphazene Species

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Complex *trans*-$[Mo(N_2)_2(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) reacts with $NN{=}CHCOOEt$ in benzene solution to afford benzene-azomethane, $Ph—N{=}N—CH_3$, as the main organic product. However, the phosphazene species $Ph_2P(N_2CHCOOEt)(CH_2CH_2)P(N_2CHCOOEt)Ph_2$ is formed by irradiating a *THF* solution of *trans*-$[W(N_2)_2(dppe)_2]$ in the presence of ethyldiazoacetate; in moist solution, the phosphazene bonds undergo a partial hydrolysis, and the phosphonium species $[Ph_2P(NHNCHCOOEt)(CH_2CH_2)P(NHNCHCOOEt)Ph_2]^{2+}$ appears to be formed.

(Keywords: Catalysis; Dinitrogen complexes; Ethyldiazoacetate)

Untersuchungen zu den Reaktionen der Distickstoff-Komplexe trans-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ *(M = Mo oder W) mit Ethyldiazoacetat: Die Bildung einer Azoverbindung und eines Phosphazens*

Die Komplexe *trans*-$[Mo(N_2)_2(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) reagieren mit $NN{=}CHCOOEt$ in benzolischer Lösung zu $Ph—N{=}N—CH_3$ als organischem Hauptprodukt. Andererseits wird bei der Bestrahlung von *trans*-$[W(N_2)_2(dppe)_2]$ in *THF*-Lösung in der Gegenwart von Ethyldiazoacetat das Phosphazen $Ph_2P(N_2CHCOOEt)(CH_2CH_2)P(N_2CHCOOEt)Ph_2$ gebildet; in feuchter Lösung erleidet die Phosphazen-Bindung eine teilweise Hydrolyse und die Phosphonium-Spezies $[Ph_2P(NHNCHCOOEt)(CH_2CH_2)P(NHNCHCOOEt)Ph_2]^{2+}$ scheint gebildet zu werden.

Introduction

The study of the activation of unsaturated species, such as isocyanides and alkynes by electron-rich dinitrogen-binding centres has been the object of our attention and, e.g., the former are strongly activated towards electrophilic attack[1,2] whereas the latter undergo isomerization reactions involving 1,2- or 1,3-hydrogen shifts[3,4].

We are now extending this type of study to different species—diazo compounds—which have not yet been studied in detail, although diazo ligands may be derived[5] from ligating dinitrogen in complexes of the type *trans*-[$M(N_2)_2(dppe)_2$] (**A**, M = Mo or W), thus being potential important intermediates in the conversion of N_2 into organonitrogenated species.

In the present work, we report our preliminary results of the study of the reactions of complexes **A** with ethyldiazoacetate.

Experimental

Experiments were carried out in the absence of air, through standard high-vacuum and inert gas flow techniques. Solvents were dried by standard procedures.

Infrared spectra were recorded on a 577 or 457 Perkin-Elmer Grating Infrared Spectrophotometer. ^{1}H-NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer (100 MHz).

Complexes *trans*-[$M(N_2)_2(dppe)_2$] (M = Mo[10] or W[11]) were prepared by published methods. Ethyldiazoacetate was used as purchased from Aldrich and Fluka.

Gas chromatography/mass spectrometry experiments were carried out in a Carlo Erba 4160 chromatograph equipped with a ChromPak SIL 5 column, and a Varian MAT 112 S apparatus.

*Formation of Ph*N=N*Me*

In a typical experiment, $N_2CHCOOEt$ (1.0 cm^3, 10.4 mmol) was added to a solution of *trans*-[$Mo(N_2)_2(dppe)_2$] (1.10 g, 1.16 mmol) in benzene (80 cm^3) at room temperature and under dinitrogen, and the resulting homogeneous system was stirred for ca. 10 h. Addition of pentane (500 cm^3) leads to the deposition of a solid which is filtered off. The solution is concentrated under vacuum to ca. 100 cm^3 and analysed by gas chromatography/mass spectrometry.

Formation of the Phosphazene Species $Ph_2P(N_2CHCOOEt)(CH_2CH_2)P(N_2CHCOOEt)Ph_2$ (B)

Ethyldiazoacetate (0.298 cm^3, 2.86 mmol) was added to a solution of *trans*-[$W(N_2)_2(dppe)_2$] (0.450 g, 0.434 mmol) in *THF* (40 cm^3). The solution was left in an argon atmosphere under the irradiation from a 150 W and another 100 W tungsten filament bulb. After stirring for two days, the solution was concentrated and compound **B** precipitated upon addition of diethyl ether; it was washed by a mixture of *THF*/diethyl ether (with a volume ratio of 1 : 2) and dried under vacuum, yielding a white solid (0.050 g, 0.080 mmol, 18% yield).

Compound **B** may also be prepared from reaction of the parent N_2 complex with a lower excess of ethyldiazoacetate (1 : 3.5) in an argon atmosphere and under the above mentioned irradiation conditions. The white solid **B** separated out of the solution upon great concentration carried out after two days reaction (the yield appears to be slightly lower than that obtained in the previous procedure).

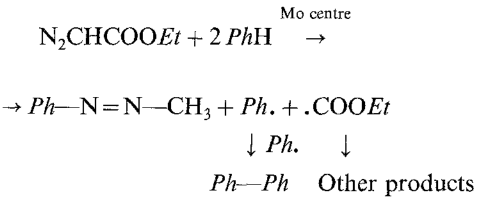
Results and Discussion

Reaction of trans-$[Mo(N_2)_2(\mathit{dppe})_2]$ (**A**, M = Mo) *with Ethyldiazoacetate in Benzene: Formation of* $\mathit{Ph}N{=}N\mathit{Me}$

The reaction of complex **A** (M = Mo) with $N_2CHCOO\mathit{Et}$ (in a tenfold excess) was carried out in benzene, by stirring the system for 10 h at ambient temperature. Some yet unidentified complex products were removed by precipitation upon addition of pentane, and the filtered solution was concentrated under vacuum and analysed by gas chromatography/mass spectrometry.

Benzene-azomethane, $\mathit{Ph}N{=}N\mathit{Me}$, was the main detected organic product and its formation may conceivably result from the reaction of benzene ($\mathit{Ph}N{=}N\mathit{Me}$ was not detected if the reaction was carried out in a different solvent such as *THF*) with $N_2CHCOO\mathit{Et}$, both activated by a molybdenum centre derived from complex **A** (M = Mo) by N_2 evolution which is known to occur readily in solution.

Ph—Ph was also a detected product of the reaction which may possibly occur according to the overall reaction scheme (1).



$$N_2CHCOO\mathit{Et} + 2\,\mathit{Ph}H \xrightarrow{\text{Mo centre}}$$

$$\to \mathit{Ph}{-}N{=}N{-}CH_3 + \begin{array}{c}\mathit{Ph}.\\ \downarrow \mathit{Ph}.\\ \mathit{Ph}{-}\mathit{Ph}\end{array} + \begin{array}{c}.COO\mathit{Et}\\ \downarrow\\ \text{Other products}\end{array} \qquad (1)$$

The reaction, which does not occur in the absence of complex **A** (M = Mo) and under identical experimental conditions, may have a catalytic character since the consumption of $N_2CHCOO\mathit{Et}$ was monitored by solution infrared spectroscopy until a total of (at least) six molar excess relative to the initial amount of metal complex.

These results also appear to illustrate a new type of reaction of a diazo compound activated by a nitrogen fixation metal centre, an azo species being formed with the involvement of the aromatic solvent through a reaction which leads to C—N bond formation.

The previously known examples of reactivity of diazo ligands (derived from ligating N_2, at a metal centre related to that of the present study) involve the protonation (by HBr) of the neutral complex $[WBr_2(NNC\mathit{Me}_2)(P\mathit{Me}_2\mathit{Ph})_3]$ to afford the organohydrazine $H_2NNHCBr\mathit{Me}_2$ (which decomposes to dimethylketazine $\mathit{Me}_2C{=}N{-}N{=}C\mathit{Me}_2$ and N_2H_4 + HBr)[6], and the nucleophilic attack, e.g., by *Me*Li, at the complex cation $[WBr(NNCH_2)(\mathit{dppe})_2]^+$ to give an alkyldiazenido compound $[WBr(NNCH_2CH_3)(\mathit{dppe})_2]$[7].

Reaction of trans-$[W(N_2)_2(dppe)_2]$ (**A**, *M* = W) *with Ethyldiazoacetate in THF: Formation of a Phosphazene*

If a solution of complex **A** (*M* = W) with an excess of ethyldiazoacetate—in *THF* and under argon—is irradiated by tungsten filament light, a white species **B** is formed in which the presence of the tungsten metal was not detected by atomic absorption.

On the basis of infrared, ^{1}H-NMR and microanalytical data, this species is formulated as the phosphazene compound $Ph_2P[{=}N{-}N{=}C(H)COOEt]CH_2CH_2P[{=}N{-}N{=}C(H)COOEt]Ph_2$, (**B**), formed (reaction 2) by the addition of one ethyldiazoacetate molecule to each of the phosphorus atoms of a *dppe* molecule derived from decomposition of the bisdinitrogen complex. Formation of phosphazenes from addition reactions of organic diazo compounds is a known preparative route for those species[11a].

$$Ph_2PCH_2CH_2PPh_2 + 2\,N_2CHCOOEt \rightarrow Ph_2P(N_2CHCOOEt)CH_2CH_2P(N_2CHCOOEt)Ph_2 \qquad (2)$$

Compound **B** exhibits three strong bands in the infrared spectrum at 1 680, 1 530 and 1 175 cm^{-1} which are assigned to $\nu(C{=}O)$, $\nu(C{=}N)$ and $\nu(P{=}N)$, respectively. The values lie in the expected ranges for these stretching vibrations, namely the usual observed one for $\nu(P{=}N)$ at 1 147–1 344 cm^{-1} in the phosphazene species $Ph_3P{=}N{-}\cdots$[8a]. Any phosphorous ylid species does not appear to be formed since no infrared band is observed in the region 1 200–1 220 cm^{-1} [as it is usually observed for $\nu(P{=}C)$ in these compounds[8b]]; the formation of such a species could not be ruled out *a priori* since a diazo compound may be a source of a carbene which may add to the phosphorus atom, although this normally occurs only in the presence of a Cu(I) salt, for instance in the known reaction[8b]

$$Ph_3P + NN{=}CR_2 \xrightarrow{Cu^+} Ph_3P{=}CR_2 + N_2.$$

Table 1. *Physical data for the phosphazene compound* $Ph_2P(N_2CHCOOEt)(CH_2CH_2)P(N_2CHCOOEt)Ph_2$

Colour	White
Infrared Data[a]	1 680 s [$\nu(C{=}O)$], 1 528 ms [$\nu(C{=}N)$], 1 178 ms [$\nu(P{=}N)$]
Elemental Analysis[b]	C 64.8 (65.2), H 6.0 (5.8), N 8.3 (8.9)

[a] In nujol mull.

[b] Theoretical values in parenthesis.

The ^{1}H-NMR spectrum of compound **B** in $CDCl_3$ shows the expected N_2CHCOO*Et* resonance at δ 3.08 ppm, and the methylene and methyl proton resonances of the ethyl group appear as the expected quartet (4.26 ppm) and triplet (1.27 ppm) with $^3J_{H-H} = 7.0$ Hz (Table 2).

Table 2. ^{1}H-*NMR data*[a] *for the phosphazene*
Ph$_2$P(N_2CHCOO*Et*)(CH_2CH_2)P(N_2CHCOO*Et*)*Ph*$_2$ (**B**),
and the derived phosphonium species
[*Ph*$_2$P(NHNCHCOO*Et*)(CH_2CH_2)P(NHNCHCOO*Et*)*Ph*$_2$]$(OH)_2$ (**C**)

Compound	δ	Integration	Assignment
B	8.0–7.1 m	20	—C_6H_5 (20)
	4.26 q[b]	4	—CH_2CH_3 (4)
	3.08 s	2	—CHCOO*Et* (2)
	3.2–1.7 m	4	—CH_2CH_2— (4)
	1.27 t[b]	6	—CH_2CH_3 (6)
C	8.0–7.1 m[c]	20	—C_6H_5 (20)
	6.94 s	1	OH (2)
	6.6 m, br	2	—NH (2)
	4.24 q[b]	3.5	—CH_2CH_3 (4)
	2.47 d[d]	2	—CHCOO*Et* (2)
	3.2–2.3 m, br	5	—CH_2—CH_2— (4)
	1.25 t[b]	7	—CH_2CH_3 (6)

[a] In $CDCl_3$, δ values in ppm relative to *TMS*.

[b] $^3J_{H-H} = 7$ Hz.

[c] Resonances assigned to 1/2 *THF* were observed at δ 3.69 (m) and δ 1.80 (m) ppm (each of them integrating for two protons) for a sample obtained from complex **B** with 1/2 *THF* of crystsallization.

[d] $^4J_{H-H} = 2$ Hz.

If an undried solution of compound **B** is left standing for a few days, one can follow the disappearance of the resonance at 3.08 ppm (assigned to N_2CHCOO*Et*) in the ^{1}H-NMR spectrum with concomitant growing of other resonances at 2.47 (doublet), 6.6 (broad), and 6.94 ppm (singlet). Upon D_2O addition, the doublet at 2.47 ppm coalesces into a singlet with disappearance of the other two mentioned resonances. If the reaction (2) is carried out in moist *THF*, this new species (with the three mentioned resonances) is also formed and it displays in the infrared spectrum a strong and broad band at 3420 cm^{-1} with a shoulder at 3320 cm^{-1}.

These results suggest that the phosphazene **B** is undergoing a partial hydrolysis reaction in moist solution, yielding probably the phosphonium species $[Ph_2P(\text{—NH—N}=CHR)(CH_2CH_2)P(\text{—NH—N}=CHR)Ph_2](OH)_2$ (**C**, where $R = COOEt$) with single P—N bonds, according to equation (3).

$$Ph_2P(N_2CHR)(CH_2CH_2)P(N_2CHR)Ph_2 + 2\,H_2O \rightarrow$$
$$\rightarrow [Ph_2P(NHNCHR)(CH_2CH_2)P(NHNCHR)Ph_2](OH)_2 \qquad (3)$$

Hydrolysis reactions of phosphazenes with partial or even complete P = N bond cleavage are known to occur, their extent being largely dependent on the nature of the other groups involved[8a].

The doublet at 2.47 ppm may be assigned to NHNC**H**R which is coupled ($^4J_{H-H} = 2$ Hz) to the proton N**H**NCHR; the latter shows a broad resonance as usually observed for protons attached to a nitrogen atom. The coupling between both resonances at 2.47 and 6.6 ppm was evidenced by D_2O addition (see above) and the easy proton exchange with D_2O also agrees with a NH resonance for 6.6 ppm. The singlet resonance at 6.94 ppm may be assigned to the hydroxide ion in the free state, since bonding of this species to phosphorus should lead to coupling between the O**H** proton and the ^{31}P nucleus.

Conclusion

The results of the present study suggest that diazo compounds may be susceptible to activation by dinitrogen-binding metal centres of the type $[Mo(dppe)_2]$ which induce the reaction towards benzene with formation of an aromatic C—N bond and conversion into an azo species. Incidentally, this study may be of significance in the field of application of dinitrogen complexes in catalysis which, although very promising (see e.g. the ready generation of an unsaturated metal centre upon N_2 evolution), still remains to be developed; however, examples are known of dinitrogen complexes (mainly of a group VIII metal centre) which may behave as catalyst precursors for alkene hydrogenations, isomerizations and polymerizations[9].

Nevertheless, the generality of these observations has yet to be proved through the extension of this type of study to other diazo compounds.

Photochemical decomposition of the related metal centre $[W(dppe)_2]$ appears to occur under more drastic conditions, and the diazo compound—in a different solvent (*THF*) where the abovementioned reaction cannot occur—reacts with the phosphine (possibly in the free state) to afford a phosphazene species.

Attempts to isolate and characterize intermediate complexes in those reactions are under way, and this type of investigation is also being extended to other dinitrogen-binding metal centres.

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