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The Reaction Product between *aci*-Nitromethanatobis(triphenylphosphine)Cu(I) and Acetone and its Structure

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Series of mixed complexes of Cu(I) with dinitrophenylmethane,[1] nitrophenylmethane[2] and nitromethane have been recently obtained in high yield from aryl copper(I) compounds, in the presence of tertiary phosphines (triphenylphosphine, bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane) or heterycyclic nitrogen donors (2,2′-bipyridine, 1,10-phenanthroline, pyridine, γ-picoline, quinoline). Among them the triphenylphosphine derivatives $(PPh_3)_2CuB$ (B = conjugate base of the nitrocompounds) are the most stable complexes and can be stored unchanged for days in the air at room temperature. A very different behaviour has been observed, however, in the recrystallization from hot acetone of these complexes. Only the complexes of dinitrophenylmethane could be recrystallized unchanged, while that of nitrophenylmethane gave as main product $(PPh_3)_2CuNO_2$ [2] and another new complex of Cu(I) was obtained from the nitromethane derivative. The latter will be described in this note.

Reaction of the *aci*-Nitromethanatobis(triphenylphosphine)Cu(I) with Acetone

In refluxing acetone, $(PPh_3)_2CuNM$, (I), darkens slowly also under nitrogen with formation of a little brown precipitate. From the filtered yellow solution, pale yellow crystals are formed by evaporation. Such crystals, (II), show a slight but constant analytical difference with respect to the parent compound (I): calcd for $C_{37}H_{32}CuNO_2P_2$: C 68.56. H 4.98, N 2.16, Cu 9.80; found for (I): C 69.2, H 4.92, N 2.03, Cu 9.6; found for (II): C 67.7, H 5.23, N 1.90, Cu 9.0%. This variation could be attributed to acetone of crystallization (calcd for $C_{40}H_{38}CuNO_3P_2$: C 68.02; H 5.43; N 1.98; Cu 9.00%). However the IR spectrum of (II) does not show any band ascribable to $\nu_{C=O}$ stretching. Furthermore, in comparison with the spectrum of complex (I), a new broad band is present at *ca.* 3240 cm^{-1} and the medium or strong bands at 1250, 1023 and 1004, 952, 705 cm^{-1}, attributed to ν_{asNO_2}, r_{CH_2}, ν_{sNO_2} and ω_{CH_2} respectively on the basis of the spectrum of sodium nitromethane,[3] have disappeared. The NMR spectra in $CDCl_3$ of the two compounds are also very different: (I) shows only a singlet methylene peak at 5,65 τ besides the phenyl peak centered at 2.7 τ; (II) presents a sharp singlet at 8.65 τ, two singlets of about the same area at 3.7 and 3.3 τ and the phenyl peak centered at 2.6 τ. An accurate quantitative analysis of these peaks could not be performed, because the complexes react with the solvent and they decrease rapidly, while new peaks appear in the case of compound (II). Among these new peaks the principal is that of free acetone (7.85 τ). The formation of acetone in quantities rapidly increasing with the time was also confirmed by GLC measurements of chloroform solutions of (II).

The above results suggest that both acetone and complex (I) are substantially modified in complex (II). The reaction could be formally similar to the known base catalyzed addition of aliphatic nitrocompounds to carbonyl groups to give nitroalcohols or α, β-unsaturated nitroalcohols.[4] The X-ray structure analysis of (II) was undertaken with the aim to prove this hypothesis.

Structure of the Reaction Product

$C_{40}H_{38}CuNO_3P_2$, triclinic, space group P$\bar{1}$, with cell parameters a = 13.57(1), b = 16.09(1), c = 13.16(1) Å, α = 55.2(1), β = 123.3(1), γ = 123.8(1)°, d_s = 1.28 g/cm^3, d_c = 1.27 g/cm^3 with Z = 2, μ = 7.4 cm^{-1}, $\mu \cdot r$ = 0.09, the conventional R-factor was 0.076 for 2239 independent reflections after anisotropic least-squares refinement for all the atoms. The hydrogen atom contribution was not included. Three-dimensional intensity data were collected on a Siemens diffractometer by the $\theta - 2\theta$ scan technique using MoKα radiation to a maximum 2θ angle of 52°. A view of the molecule is shown in the Figure, together with some bond lengths and angles of interest. The geometry around the copper atom is similar to those found in nitro–copper complexes[5,6] but with two different Cu–O distances, 2.27(1) and 2.11(1) Å. Analogously the Cu–P bond lengths of 2.230(5) and 2.247(3) Å and the angle $\widehat{PCuP}$ of 131.6(2)° are close to the values found for $(PPh_3)_2CuON{:}C(NO_2)Ph$, falling in the range of $(PPh_3)_2CuL$ compounds.[6] The geometry and the mutual orientation of the atoms in the $(PPh_3)_2CuO_2N$ grouping are nearly the same in this and in the above mentioned compound.[6] The $O_2N{:}C(H)C\leqslant$ group is nearly planar

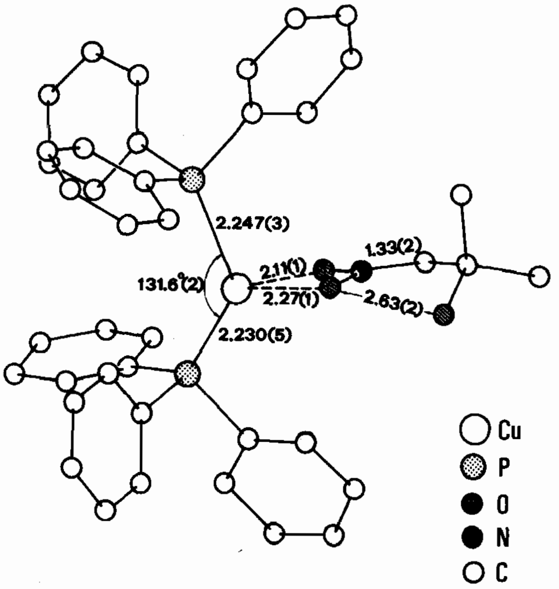
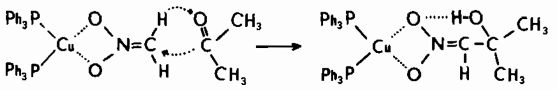


Figure. A view of the molecule with some bond lengths and angles of interest.

with displacement of its atoms of ± 0.01 Å from the mean plane, the O atom of the hydroxy group being displaced 0.08 Å. It is interesting to observe that the hydroxy group forms a hydrogen bond with the oxygen atom of the nitro group, the O···O distances being 2.63(2) Å (see Figure).

Conclusions

The structural results show that compound (II) may be considered as the product of the reaction between $(PPh_3)_2Cu^IO_2N{:}CH_2$ and acetone, according to the scheme:



The structure (II) justifies both the reported analytical data and the spectral variations.

The corresponding reaction for the free nitromethane requires basic conditions, that is the formation of the *aci*-nitro form which is preexistent in complex (I). The reported reaction explains also why no change upon recrystallization from acetone occurs in the case of the corresponding complex deriving from dinitrophenylmethane, in which no active hydrogen is present. As for the phenylnitromethane derivative the reaction with acetone must be considered competitive with the thermal cleavage of the C=N double bond, which also occurs on heating in other solvents. Since the final product is $(PPh_3)_2\cdot CuNO_2$, the latter reaction is preferred under these conditions.

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