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Preliminary communication

INTERMEDIATES IN INSERTION REARRANGEMENTS: A π-BONDED IMINOACYL—METAL COMPLEX

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Summary

The complex, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNC_6H_5)$, has been synthesized. It crystallizes in the space group $P2_1/c$; a 7.789(4), b 6.810(3), c 26.754(15) Å, β 91.91°, $Z = 4$. An X-ray crystal structure analyses shows the presence of a π-bonded iminoacyl group. Pertinent internuclear separations are Mo—C = 2.108(5), Mo—N = 2.142(4) and C=N = 1.232(6) Å. The product is believed to be formed by isocyanide insertion into a molybdenum—methyl bond with incorporation of the nitrogen atom into the coordination sphere of the molybdenum atom. It is suggested that similar π-bonded species may be important intermediates in the mechanisms of carbonyl insertion rearrangements.

We have recently shown that organometallic anions containing isocyanide ligands readily react with the molecules RX (R = Group IV substituent, X = halide) to produce complexes in which the R group is attached directly to the metal atom [1]. However, when R is a methyl group, the initial reaction is often followed by facile isocyanide insertions [2]. We report, here, the X-ray crystal structure analysis of one of these insertion products, which is shown to contain a π-bonded iminoacyl group.

Reaction of the anion* $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNC_6H_5^-$ (I) with methyl iodide in THF produces the compound $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CNC_6H_5)$ (II). Upon removal of the THF, the pure product can be obtained by hexane extraction and crystallization. Compound II crystallizes in the space group $P2_1/c$*. 2012 reflections with $F^2 > 3\sigma(F^2)$ were collected in the scan range $2\theta = 0$—55°**. The structure was solved by the conventional heavy atom methods. Full matrix least squares anisotropic refinement on all nonhydrogen atoms and coordinate refinement on all 13 located hydrogen atoms converged to the

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*Prepared by reduction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNC_6H_5I$ with Na(Hg) in THF.

**Intensity data were collected on a Picker FACS-1 using monochromatized molybdenum radiation. Due to thermal instability crystal data were collected at −22°C.

final discrepancy indices $R_w = 0.040$. The molecular structure is shown in Fig. 1. In addition, to a normal *pentahapto*-cyclopentadienyl ring and two linear carbonyl groups, we observe an iminoacyl ($CH_3CNC_6H_5$) group, that is π-bonded to the metal atom. Pertinent bond distances and angles are listed in Tables 1 and 2. Structurally, it resembles a π-coordinated acetylene. When coordinated, acetylenes are nonlinear and are characterized by a folding angle, β, as shown in Fig. 2A. This angle ranges from approximately 138—165° for aryl [7] and alkyl [8] acetylenes. These compare favourably with the angles $\beta_1 = 138.7(6)°$ and $\beta_2 = 134.9(5)°$ for this π-bonded iminoacyl group (Fig. 2B).

Most iminoacyl groups bond to metal atoms in a σ fashion, in which only the carbon atom of the imine group is bonded to the metal atom. A structural investigation of the compound *trans*-$PtI(CCH_3{=}N\text{-}p\text{-}C_6H_4Cl)(P(C_2H_5)_3)_2$ (III) shows this arrangement. For this complex, the angles β_3 and β_4, in Fig. 2C, are 125.4 and 115.4°, respectively [5]. Relevant internuclear distances are Pt—C = 2.027(11), Pt—N = 3.042(10) and C=N = 1.287(13) Å. The very long Pt—N distance precludes any significant bonding interaction between these atoms. For the π-bonded iminoacyl complex, reported here, internuclear distances are Mo—C(4) = 2.108(5), Mo—N = 2.142(4) and C(4)=N = 1.232(6) Å. In this case, the nitrogen atom forms a strong bond to the molybdenum atom. Furthermore, upon adopting the π-bonded configuration, the β angles increase

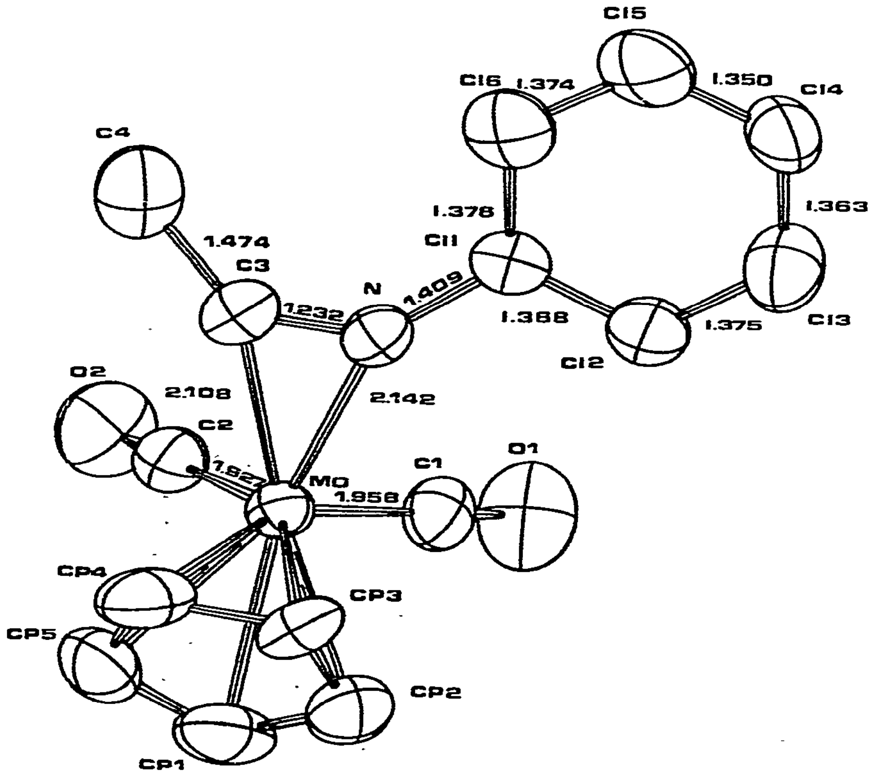


Fig. 1. Molecular structure of compound II.

TABLE 1

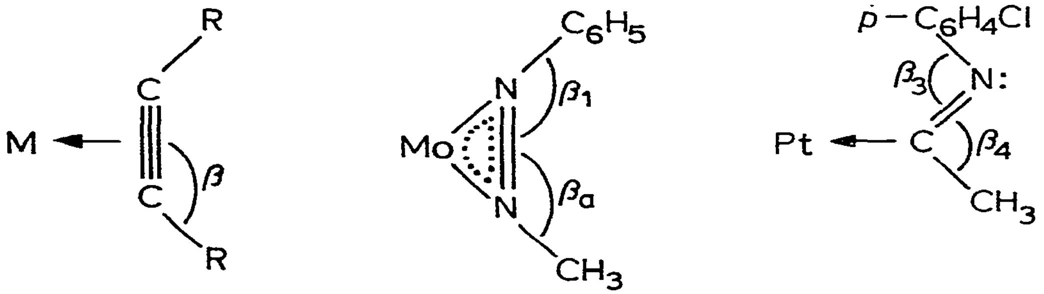
PERTINENT BOND DISTANCES

Atoms	Distance (Å)	Atoms	Distance (Å)
Mo—C1	1.958(6)	CP3—CP4	1.393(9)
Mo—C2	1.927(6)	CP4—CP5	1.395(9)
Mo—C3	2.108(5)	C1—O1	1.145(6)
Mo—N	2.142(4)	C2—O2	1.158(6)
Mo—CP1	2.303(6)	C3—C4	1.474(8)
Mo—CP2	2.336(6)	N—C11	1.409(6)
Mo—CP3	2.390(6)	C11—C12	1.368(8)
Mo—CP4	2.372(6)	C11—C16	1.376(7)
Mo—CP5	2.319(6)	C12—C13	1.375(8)
CP1—CP2	1.413(9)	C13—C14	1.363(9)
CP1—CP5	1.390(9)	C14—C15	1.350(9)
CP2—CP3	1.388(9)	C15—C16	1.374(9)

TABLE 2

PERTINENT BOND ANGLES

Atoms	Angle (degrees)	Atoms	Angle (degrees)
C1—Mo—C2	76.5(2)	CP2—CP3—CP4	108.4(7)
C3—Mo—N	33.7(2)	CP3—CP4—CP5	107.6(7)
Mo—C1—O1	176.9(5)	CP4—CP5—CP1	108.9(6)
Mo—C2—O2	178.8(5)	N—C3—C4	134.9(6)
Mo—C3—C4	150.3(5)	C3—N—C11	138.7(5)
Mo—N—C11	148.2(3)	N—C11—C12	117.3(5)
Mo—C3—N	74.7(3)	N—C11—C16	123.7(5)
Mo—N—C3	71.7(3)	C12—C11—C16	119.0(5)
Mo—CP1—CP2	73.5(3)	C11—C12—C13	120.8(6)
Mo—CP1—CP5	73.1(3)	C12—C13—C14	120.8(6)
CP2—CP1—CP5	107.0(6)	C13—C14—C15	119.2(6)
CP1—CP2—CP3	108.1(6)	C14—C15—C16	121.9(6)
		C15—C16—C11	119.2(6)



(A) (B) (C)

Fig. 2. Structure of (A) a coordinated acetylene group, (B) the iminoacyl group of compound II and (C) the (CCH_3=N-p-C_6H_4Cl) group of compound III.

and the CN multiple bond is strengthened, as is shown by the shortening of the CN internuclear distance. In sum, it becomes more like a π-bonded acetylene. The strenghtening of the CN bond is also manifested in an increase in the frequency of the stretching vibration [2].

This complex is believed to be formed by initial alkylation of the anion I, at the molybdenum atom [2]. This is followed by a facile isocyanide insertion, and incorporation of the nitrogen atom into the coordination sphere of the molybdenum atom. It is clear that the π-bonded arrangement is an important structural form for metal—iminoacyl complexes and probably also for metal—acyl complexes [6]. In fact, the ability of the heteroatom, N or O, to engage in complimentary bonding to the metal atom may be an important factor in determining this course of the insertion rearrangement, especially, when this occurs in poor donor solvents.

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