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Preliminary communication

SYNTHESES OF ORGANOMETALLIC COMPOUNDS CONTAINING IMINOACYL LIGANDS. REACTIONS OF METAL CARBONYL ANIONS WITH IMIDOYL HALIDES

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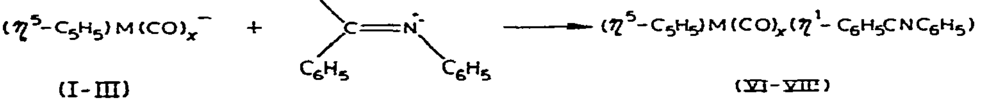
Summary

Reactions of metal carbonyl anions with imidoyl halides provide a convenient route for the preparation of organometallic complexes containing both η^1- and η^2-iminoacyl ligands. With poorer nucleophiles such as tetracarbonyl cobaltate anion, coupling of imidoyl groupings becomes important. This is illustrated by the molecule $Co_2(CO)_5(P(CH_3)_2C_6H_5)\{(C_6H_5)CN(C_6H_5)\}_2$ which has been crystallographically analyzed.

Recent studies of isocyanide insertion reactions have revealed new and unusual features of the coordination behavior of iminoacyl ligands [1—4]. This ligand has now been shown to bond effectively in both η^1- and η^2-structural arrangements. To further our studies of both structural and reaction chemistry of this ligand, we wish to report that we have now identified a new route for their preparation. It appears to have considerable scope and generality, but is subject to certain limitations as will be described below.

Presently established routes for the synthesis of iminoacyl ligands include: (1) insertion of isocyanides into metal—carbon bonds [5]; (2) nucleophilic attack on isocyanide ligands [5]; and (3) oxidative additions of imidoyl chlorides [6]. We have now found that metal carbonyl anions react with imidoyl chlorides to produce good yields of new complexes containing the iminoacyl ligand.



(1)

(I-III)

(VI-VIII)

(I,VI · M = W, $x = 3$, II,VII.M = Fe, $x = 2$ III VIII-M = Ni $x = 1$)

Each of the anions I—III readily reacts with $(C_6H_5)(Cl)C{=}N(C_6H_5)$ through halide displacement to produce the compounds VI—VIII* (eq 1). Irradiation of VI or VII causes elimination of one molecule of carbon monoxide to form the new compounds IX and X* (eq. 2).

$$\underset{(VI-VII)}{(\eta^5\text{-}C_5H_5)M(CO)_x(\eta\ \text{-}C_6H_5CNC_6H_5)} \xrightarrow[-CO]{h\nu} \underset{(IX-X)}{(\eta^5\text{-}C_5H_5)M(CO)_{x-1}(\eta^2\text{-}C_6H_5CNC_6H_5)} \qquad (2)$$

While the former complexes evidently contain the more common η^1-structural arrangement of the iminoacyl ligand, we believe complexes IX and X possess the η^2-structural arrangement [2]. The only organometallic compound that was isolated from the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ (IV) with $(C_6H_5)(Cl)C{=}N(C_6H_5)$ was $(\eta^5\text{-}C_5H_5)Mo(CO)_2(C_6H_5)CN(C_6H_5)$ (XI) which we believe also contains an η^2-iminoacyl ligand. Evidently, this reaction has proceeded like the others except that the initially formed analog of VI spontaneously eliminated carbon monoxide to form XI.

The reaction of $Co(CO)_4^-$ (V) with $(C_6H_5)(Cl)C{=}N(C_6H_5)$ is considerably more complicated. It proceeds only very slowly to produce a new compound which analyzes as $Co_2(CO)_6\{(C_6H_5)CN(C_6H_5)\}_2$ (XII)**. Its infrared spectrum shows a bridging carbonyl absorption at 1810 cm^{-1}. We chose to establish the molecular structure of XII by X-ray crystallographic techniques, but were unable to obtain crystals suitable for diffraction analyses. As a result, we have prepared the derivative $Co_2(CO)_5(P(CH_3)_2C_6H_5)\{(C_6H_5)CN(C_6H_5)\}_2$ (XIII) formed by the reaction of XII with one equivalent of $P(CH_3)_2(C_6H_5)$. The molecular structure of XIII is shown in Fig. 1***. For clarity, the four phenyl rings of the $\{(C_6H_5)CN(C_6H_5)\}_2$ grouping have been omitted from the figure. In Table 1 is a list of final atomic fractional coordinates. The structure shows two mutually bonded cobalt atoms (Co—Co 2.447(1) Å). There are two linear terminal carbonyl groups bonded to each cobalt atom, a bridging carbonyl group, and a normal dimethylphenylphosphine ligand bonded to one cobalt atom (Co(1)). The most interesting feature is the bis-imidoyl ligand represented in the figure by the four atom chain C(6)—N(2)—C(5)—N(1). Only atoms C(6) and N(1) are coordinated to the cobalt atoms. N(1) is bonded solely to Co(2) while C(6) is bonded to both Co(1) and Co(2) C(6) could formally be regarded as a bridging carbenoid carbon. In effect, this bis-imidoyl ligand chelates cobalt atom Co(2) while atom C(6) simultaneously serves as a bridge. A similar bis-imidoyl carbenoid-chelating ligand bonded to a single metal atom was found in

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*Satisfactory IR, NMR, and elemental analyses have been obtained for these compounds Formulae are also supported by mass spectral analyses. Each compound shows the expected parent ion and the successive loss of each of the appropriate number of carbonyl ligands

**While the reactions of the previous anions are usually complete within 30 min, the reaction with $Co(CO)_4^-$ takes approx. 2 days.

***XIII crystallizes in the space group $P2_1/c$ a 12 189(4) b 15.749(5), c 18 874(6) Å, β 95.49(3)°, Z = 4.2524 reflections with $F_o^2 > 3\,\sigma(F_o^2)$ were collected with an Enraf-Nonius CAD-4 automatic diffractometer using Mo-K_α radiation. The structure was solved by the heavy atoms method using the Enraf-Nonius SDP program library. The final values of the residuals R and R_w were 0 061 and 0 068 respectively.

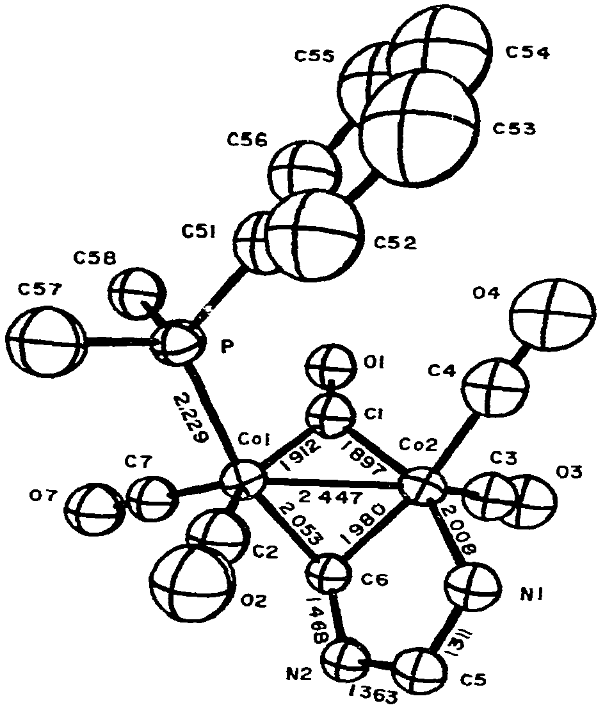

Fig 1 Molecular structure of $Co_2(CO)_5(P(CH_3)_2C_6H_5)\{(C_6H_5)CN(C_6H_5)\}_2$

$Cl_3(CO)Rh\{C(C_6H_5)N(CH_3)C(C_6H_5)N(CH_3)\}$ which was formed in the reaction of $[Rh(CO)_2Cl]_2$ with $C_6H_5(Cl)CN(CH_3)$ [7]

While various mechanisms can be proposed for the formation of XII and XIII the one we presently prefer is shown in Scheme 1.

Step 1 is a nucleophilic replacement of chloride by the tetracarbonylcobaltate anion and is analogous to the reactions of the previous anions, I–IV. Step 2 involves a nucleophilic attack of the nitrogen atom of the complex on a second molecule of imidoyl chloride. This is analogous to the well-known self-condensation reaction that has been demonstrated for C-alkyl imidoyl halides [8]. Attack of a second tetracarbonyl cobaltate anion on the carbon atom containing the previous tetracarbonyl cobalt group (step 3), is followed an elimination of carbon monoxide, formation of the cobalt—cobalt bond and the bridging carbonyl group (step 4). Finally, the nitrogen atom of the external imino group displaces carbon monoxide and coordinates to one of the cobalt atoms (step 5)

Studies have shown that acyl halides readily react with metal carbonyl anions to form complexes containing acyl ligands [9] On the other hand, vinyl halides are quite unreactive [9]. Our results show that imidoyl halides seem to have an intermediate reactivity. With stronger nucleophiles (I—IV) they react to form complexes containing iminoacyl ligands while with weaker nucleophiles (V) [9] unusual coupling reactions become important

TABLE 1

FRACTIONAL ATOMIC COORDINATES FOR $Co_2(CO)_5(P(CH_3)_2C_6H_5)\{(C_6H_5)CN(C_6H_5)\}_2$

Atom	*x/a*	*y/b*	*z/c*
Co(1)	0 08364(10)	0 20074(8)	0 17887(6)
Co(2)	−0 08845(10)	0 21328(8)	0 23512(7)
P	0 14509(21)	0 32279(16)	0 13770(14)
O(1)	0 0911(5)	0 3119(4)	0 3048(3)
C(1)	0 0507(8)	0 2645(6)	0 2604(5)
O(2)	−0 0052(6)	0 1507(5)	0 0361(4)
C(2)	0 0286(8)	0 1687(6)	0 0935(5)
O(3)	−0.1544(7)	0.1873(5)	0 3769(4)
C(3)	−0 1316(8)	0 1981(7)	0 3181(5)
O(4)	−0 1939(6)	0 3800(5)	0 2142(4)
C(4)	−0 1510(8)	0 3138(7)	0 2202(5)
O(7)	0 3043(6)	0 1312(5)	0 2009(4)
C(7)	0 2154(8)	0 1586(7)	0 1948(5)
C(57)	0 1926(9)	0 3123(7)	0 0491(6)
C(58)	0 2645(8)	0 3661(7)	0 1905(6)
N(1)	−0 1895(6)	0 1503(5)	0 1630(4)
N(2)	−0 0637(6)	0 0460(5)	0 1850(4)
C(5)	−0 1604(7)	0 0723(6)	0 1494(5)
C(6)	0 0004(7)	0 1087(6)	0 2292(4)
C(11)	−0 2848(7)	0 1880(6)	0 1227(5)
C(12)	−0 3728(9)	0.2132(7)	0 1578(6)
C(13)	−0 4635(10)	0 2524(8)	0 1160(6)
C(14)	−0 4603(10)	0 2631(8)	0 0486(7)
C(15)	−0 3761(10)	0 2399(8)	0 0120(6)
C(16)	−0.2846(8)	0 2001(7)	0 0513(5)
C(21)	−0 2285(7)	0 0150(6)	0 1010(5)
C(22)	−0 3313(8)	−0 0095(6)	0 1283(5)
C(23)	−0 4001(10)	−0 0609(8)	0 0753(7)
C(24)	−0 3657(10)	−0 0827(8)	0 0115(7)
C(25)	−0 2674(10)	−0 0616(8)	−0 0084(6)
C(26)	−0 1977(9)	−0 0110(7)	0 0374(5)
C(31)	−0 0184(7)	−0 0371(6)	0 1720(5)
C(32)	−0 0746(8)	−0.1112(7)	0.1806(6)
C(33)	−0 0273(9)	−0 1890(7)	0 1628(6)
C(34)	0 0725(9)	−0 1911(7)	0.1385(6)
C(35)	0 1311(8)	−0 1187(7)	0 1314(5)
C(36)	0 0854(7)	−0 0407(6)	0 1461(5)
C(41)	0 0445(7)	0 0707(6)	0 2990(5)
C(42)	−0 0194(8)	0 0100(6)	0 3314(5)
C(43)	0 0130(9)	−0 0211(7)	0 3988(6)
C(44)	0 1071(9)	0 0085(7)	0 4359(6)
C(45)	0 1716(9)	0 0675(7)	0 4071(6)
C(46)	0 1419(8)	0 0983(6)	0 3381(5)
C(51)	0 0512(8)	0 4117(6)	0 1283(5)
C(52)	−0 0367(11)	0.4106(9)	0 0778(7)
C(53)	−0 1144(12)	0 4812(10)	0 0731(8)
C(54)	−0 0939(9)	0 5458(9)	0 1189(8)
C(55)	−0 0130(11)	0 5472(10)	0 1708(8)
C(56)	0 0596(10)	0 4797(7)	0 1747(6)

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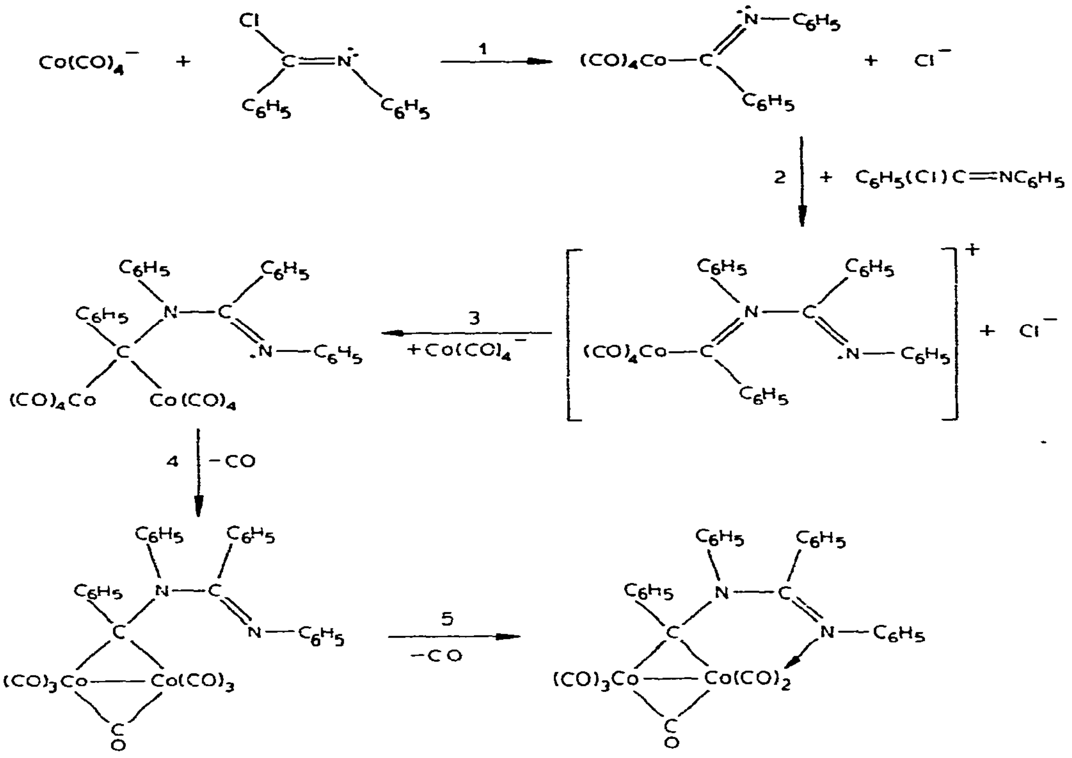

(XII)

Scheme 1

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