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

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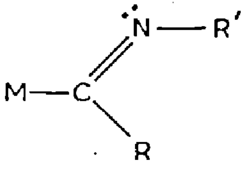
Summary

Metal carbonyl anions readily react with imidoyl halides through nucleophilic displacement of the halide atom to produce complexes containing η^1-iminoacyl ligands. However, weakly nucleophilic anions, such as tetracarbonylcobaltate, induce a head-to-tail coupling reaction of two imidoyl groupings via the incorporation of two anions. This has been established by an X-ray crystallographic analysis of the compound $Co_2(CO)_5(P(CH_3)_2C_6H_5)[(C_6H_5)CN(C_6H_5)]_2$. The bis-imidoyl ligand chelates one cobalt atom while one of the carbon atoms bridges the two mutually bonded cobalt atoms.

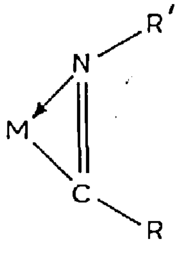
Photolytic decarbonylation of the complexes containing η^1-iminoacyl ligands may proceed by either of three processes. When the substituent on the nitrogen atom is an alkyl group, either a migration with formation of an isocyanide ligand or formation of an η^2-iminoacyl ligand can occur. When the substituent is an aryl group, *ortho*-metallation of the *N*-aryl ring occurs. This has been demonstrated by an X-ray crystallographic analysis of the compound $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$ which contains a phenyl-*N*-*p*-tolylaminocarbene ligand in which the *p*-tolyl ring is bonded to the iron atom in an *ortho* position.

Introduction

Several methods are now available for the synthesis of metal complexes containing iminoacyl ligands, (I, II). These include: (1) insertion of isocyanides



(I)



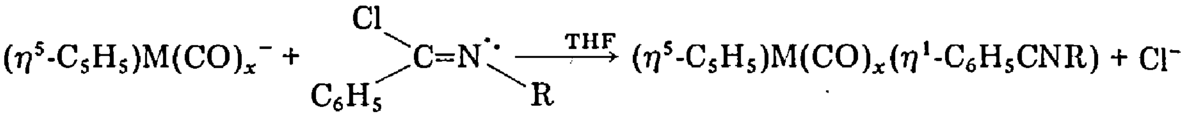
(II)

into metal—carbon bonds [1,2]; (2) nucleophilic attack on isocyanide ligands [2]; and (3) oxidative addition of imidoyl chloride molecules to metal complexes [3,4]. Here, we wish to report the results of our studies of the reactions of metal carbonyl anions with imidoyl chlorides. We have found that these reactions provide a new route for the syntheses of many metal complexes containing η^1-iminoacyl ligands, I [5].

We have recently shown that iminoacyl ligands may also exist in an unusual *dihapto*-structural arrangement, II [6]. In an effort to find other synthetic routes to these species we have investigated the photolytic decarbonylation of the *monohapto*-species.

Results and discussion

The compounds I—VII have been prepared through the reaction of the appropriate imidoyl chloride and metal carbonyl anion, eq. 1.



$$(\eta^5\text{-}C_5H_5)M(CO)_x^- + \begin{matrix} Cl & & \\ & C{=}\ddot{N} & \\ C_6H_5 & & R \end{matrix} \xrightarrow{THF} (\eta^5\text{-}C_5H_5)M(CO)_x(\eta^1\text{-}C_6H_5CNR) + Cl^- \qquad (1)$$

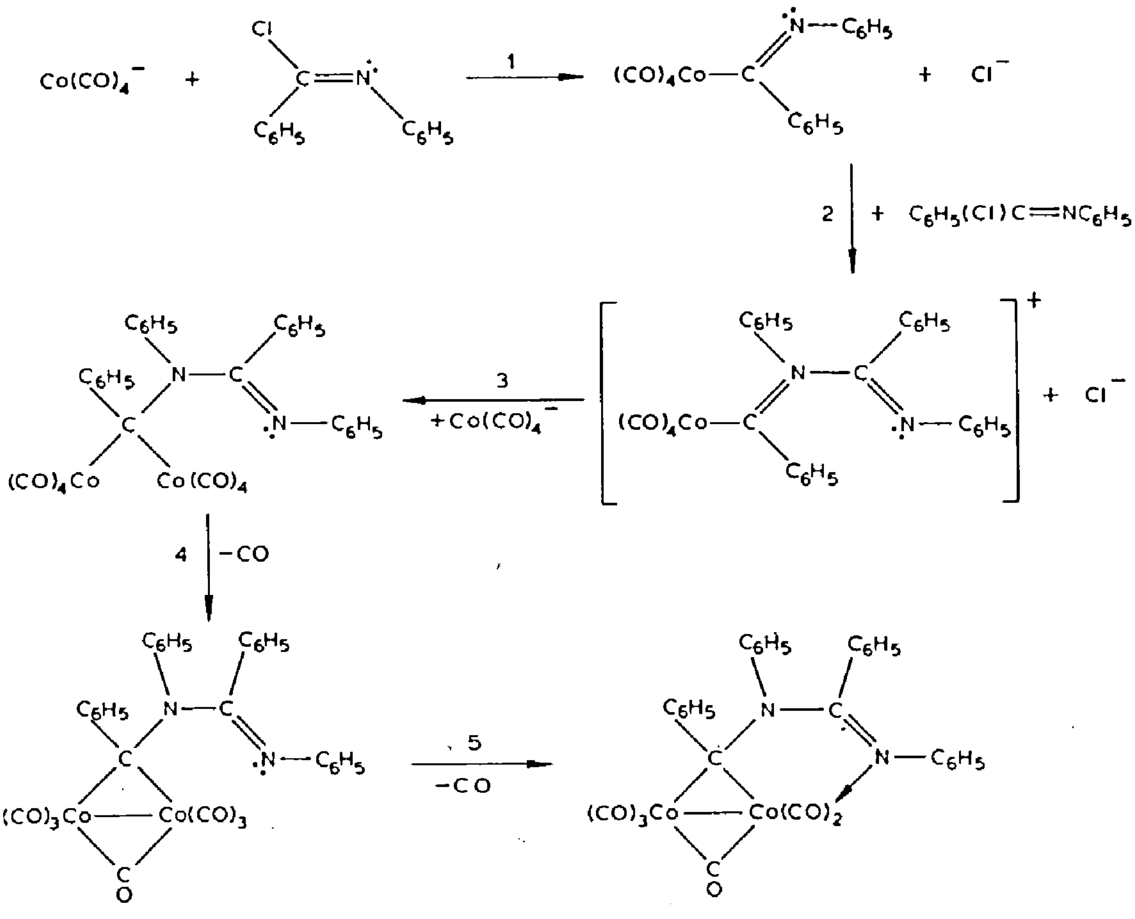
$M = Fe; x = 2; R = C_6H_5, CH_3, i\text{-}C_3H_7, p\text{-}CH_3C_6H_4$
$M = W; x = 3; R = C_6H_5, i\text{-}C_3H_7$
$M = Ni; x = 1; R = C_6H_5$

The formulations are supported by IR, ^{1}H NMR and elemental analyses. All compounds show an infrared absorption in the range 1580—1605 cm^{-1} which is characteristic of the η^1-iminoacyl ligand. The reaction appears to involve a simple halide displacement at the iminyl carbon of the imidoyl halide.

The reaction of tetracarbonylcobaltate anion with imidoyl chloride is considerably more complex. The reaction with $C_6H_5(Cl)CNC_6H_5$ proceeds slowly and produces a complex which we formulate as $Co_2(CO)_6[C_6H_5CNC_6H_5]_2$, VIII, on the basis of its IR, ^{1}H NMR, elemental analyses, and through comparison with the structure of its dimethylphenylphosphine derivative, IX, which has been analyzed crystallographically. Complexes VIII and IX each contain a bis-imidoyl grouping which appears to have been formed through a head-to-tail coupling of two imidoyl chloride molecules (cf. Fig. 1). The bis-imidoyl ligand chelates one cobalt atom while one of the carbon atoms bridges the two mutually bonded cobalt atoms. Although we have not been able to establish the mechanism of the formation of these molecules, we believe Scheme 1 is most consistent with established chemistry,

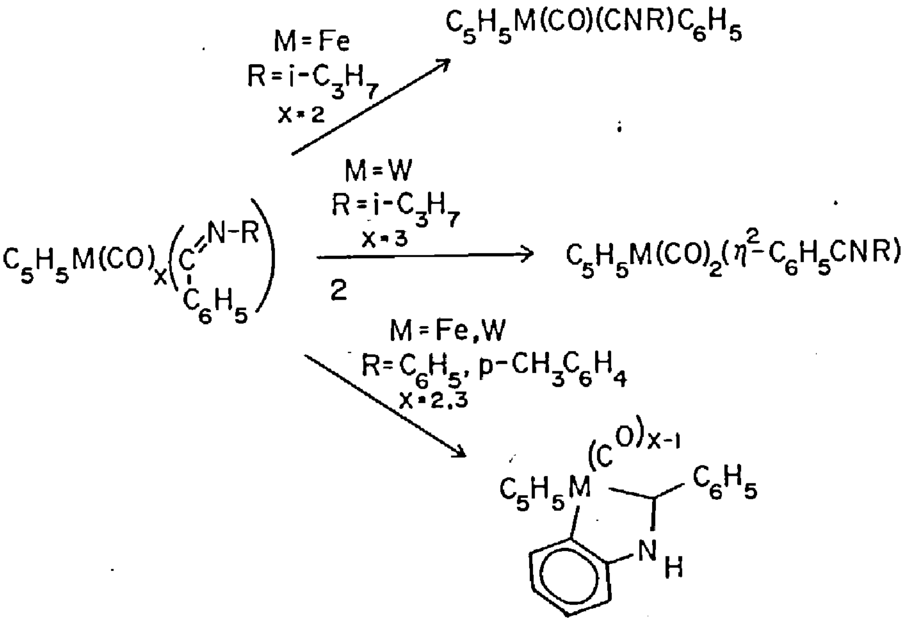
Step 1 is a nucleophilic replacement of chloride by the tetracarbonylcobaltate anion and is analogous to the reactions of the previous anions. Step 2 involves a nucleophilic attack of the nitrogen atom of the complex on a second molecule of imidoyl chloride. This is analogous to the well-known self-condensation reaction that has been demonstrated for *C*-alkyl imidoyl halides [7]. Attack of a second tetracarbonyl cobaltate anion on the carbon atom containing the previous tetracarbonyl cobalt group (step 3), is followed by an elimination of carbon monoxide, formation of the cobalt—cobalt bond and the bridging

SCHEME 1



(XII)

SCHEME 2



carbonyl group (step 4). Finally, the nitrogen atom of the external iminyl group displaces carbon monoxide and coordinates to one of the cobalt atoms (step 5).

Similar couplings of imidoyl ligands with chelating coordination to metal atoms have been reported on at least two previous occasions [9,10].

We have also investigated the photolytic decarbonylation reaction of compounds I and III—VI. We have observed three different reactions which vary depending on the metal atom and the substituent on the nitrogen atom. These reactions are summarized in Scheme 2.

Reaction 1

When R = $i\text{-}C_3H_7$, M = Fe, the product X has a strong absorption at 2115 cm^{-1} which indicates the presence of a terminally coordinated isocyanide ligand. Compound X also contains a phenyl ring and it thus appears that this compound has been formed by a phenyl migration from the iminoacyl ligand to the metal atom.

Reaction 2

On the other hand, decarbonylation of compound VI, R = $i\text{-}C_3H_7$, M = W, produced the compound XI, $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^2\text{-}C_6H_5CN\text{-}i\text{-}C_3H_7)$ which contains a η^2-iminoacyl ligand. This is supported by the appearance of a weak infrared absorption at 1675 cm^{-1} in the region which is known to be characteristic of these ligands [1,6]. As expected the isopropyl methyl groups are inequivalent, and separate resonances are seen in the ^1H NMR spectra. However, when the temperature is raised, these resonances broaden and merge into a single doublet. The coalescence temperature is approximately 102°C. The averaging process can be explained by a 180° rotation of the η^2-iminoacyl ligand. This rearrangement has been observed in the analogous molybdenum complexes [6]. In addition XI readily forms an adduct XII with tetracyanoethylene which contains a η^1-iminoacyl ligand. This reaction is also characteristic of complexes which contain η^2-iminoacyl ligands [1].

Reaction 3

When R = aryl, the products, XIII—XV are formed. These compounds do not show isocyanide absorptions and we originally believed that they also contained η^2-iminoacyl ligands [5]. However, the observation of infrared absorptions at approximately 3300 cm^{-1} has caused us to examine one of these compounds, XIV, by X-ray crystallographic methods. The results (vide infra) show that the compound contains a *N*-arylaminocarbene ligand in which the *N*-aryl ring is bonded to the metal atom at an *ortho* position. Evidently, the *N*-aryl ring reacts at the photolytically generated "vacant" site on the metal atom through an *ortho*-metallation reaction [10]. The ring hydrogen atom should be transferred to the metal atom but its final location on the nitrogen atom indicates some currently unknown hydrogen transfer process has obviously followed the *ortho*-metallation reaction. Because the infrared spectra of each of the photodecarbonylation products XIII—XV contain an absorption at approximately 3300 cm^{-1}, we believe they all contain similar *ortho*-metallated arylaminocarbene ligands.

Description of the structures

$Co_2(CO)_5P(C_6H_5)(CH_3)_2[(C_6H_5)CN(C_6H_5)]_2$, IX

The molecular structure of IX is shown in Figure 1. Each cobalt atom contains two linear carbonyl groups while one, Co(1), contains a normal $P(CH_3)_2(C_6H_5)$ ligand. The cobalt—phosphorus distance is 2.229(2) Å and is typical of that found in other cobalt—phosphine complexes, (e.g. Co—P, 2.253 Å, $CH_3CCo_3(CO)_8P(C_6H_5)_3$ [11]; 2.19 Å, $Co_2(CO)_6(P(C_4H_9)_3)_2$ and $Hg[Co(CO)_3(P(C_2H_5)_3]_2$ [12]; 2.214 Å, $As_2Co_2(CO)_5P(C_6H_5)_3$ [13]; 2.27(1) Å, $HCF_2CF_2Co(CO)_3P(C_6H_5)_3$ [14]; 2.26 Å, $Co(CO)_3(Ge(C_6H_5)_3)(P(C_6H_5)_3)$ [15]). The cobalt atoms are joined by a single bond Co(1)—Co(2) = 2.447(1) Å, and are bridged by one carbonyl ligand and one carbon atom of the $[C_6H_5CNC_6H_5]_2$ ligand. The $[C_6H_5CNC_6H_5]_2$ ligand can be described as a head-to-tail coupling of two $C_6H_5CNC_6H_5$ units. The atoms C(6), N(2), C(5), N(1), Co(2) form a metallacyclic ring. Atom N(1) is bonded solely to cobalt atom Co(2), but carbon C(6)

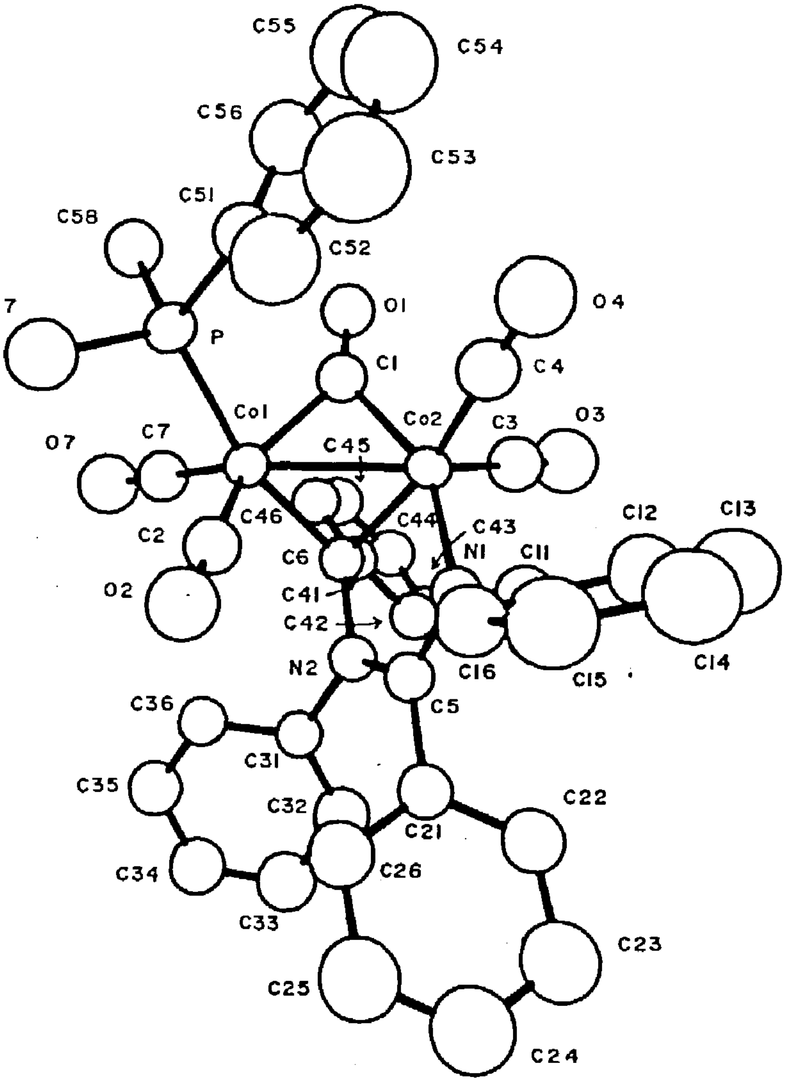


Fig. 1. An ORTEP diagram of $Co_2(CO)_5(P(CH_3)(C_6H_5))[C_6H_5CNC_6H_5]_2$ showing 50% probability ellipsoids.

(Continued on p. 258)

TABLE 1

ANALYTICAL DATA

Compound	M.p. (°C)	Yield (%)	Analyses (found (calcd.)) (%)			Infrared (cm^{-1})	^1H NMR (ppm)
			C	H	N		
$(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_5CNC_6H_5)$, I	106 (dec)	60	66.43 (67.25)	4.36 (4.23)	3.90 (3.92)	2010s, 1950s 1586m [a]	4.90 (s), 7.1 (m) [b]
$(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_5CNCH_3)$, II	87—89	38	60.19 (61.05)	4.41 (4.44)	5.12 (4.75)	2001, 1945s 1596m	3.51 (s), 5.16 (s), 7.13 (m) [b]
$(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_5CN\text{-i-}C_3H_7)$, III	109—111	32	63.24 (63.18)	5.71 (5.30)	4.25 (4.33)	2010s, 1960s, 1590w [c]	5.12(s), 7.07 (m), 1.12 (6) (d), 3.66(1) (sept) J = 6 Hz [b]
$(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_5CN\text{-}p\text{-}CH_3C_6H_4)$, IV	125—130	38	67.76 (67.94)	4.64 (4.61)	3.70 (3.77)	2000s, 1940s, 1590w [a]	2.21 (s), 4.85 (s) 6.56 (m), 7.12 (m) [b]
$(C_5H_5)W(CO)_3(\eta^1\text{-}C_6H_5CNC_6H_5)$, V	101—102	44	48.34 (49.48)	3.00 (2.95)	2.62 (2.75)	2015s, 1924s 1585w [a]	5.58 (s), 6.8 (m)
$(C_6H_5)W(CO)_3(\eta^1\text{-}C_6H_5CN\text{-i-}C_3H_7)$, VI	81—82	62	45.69 (45.13)	3.78 (3.58)	3.04 (2.92)	2015s, 2002s 1925vs, 1584w [c]	5.10(s), 3.36 (sept), 1.29 (d), J = 6.3 Hz, [d, j]; 5.26 (s) 3.72 (sept), 1.00 (d), J = 6.3 Hz; 7.01(m) [k]
$(C_5H_5)Ni(CO)(\eta^1\text{-}C_6H_5CNC_6H_5)$, VII	65.5—67	27	68.53 (68.73)	4.78 (4.55)	4.24 (4.22)	2025s, 1605w [a]	5.14 (s), 6.75 (m), 7.30 (m) [b]
$Co_2(CO)_6[C_6H_5CNC_6H_5]_2$, VIII	140 (dec)	71	61.03 (61.06)	4.16 (3.81)	4.07 [g] (4.07)	2060s, 2025vs, 2000s, 1975(sh), 1810m [a]	6.96—7.54 (m) [b]
$Co_2(CO)_5(P(CH_3)_2C_6H_5)[C_6H_5CNC_6H_5]_2$, IX	168—171	77	[f]			2440m, 1985s, 1940m, 1740m [d]	6.76—7.43 (m), 1.93 (d) [b] J(P—H) = 9 Hz

							J(P—H) = 9 Hz
$(C_5H_5)Fe(CO)(CN\text{-}i\text{-}C_3H_7)(C_6H_5)$, X	67—68	43	64.33 (65.11)	5.58 (5.81)	4.93 (4.75)	2115m, 1953w [a]	4.47 (s), 6.7—7.4 m 1.34(6) (d), 4.00(1) (sept) J = 6 Hz [b]
$(C_5H_5)W(CO)_2(\eta^2\text{-}C_6H_5CN\text{-}i\text{-}C_3H_7)$, XI	98.5—101	40	45.48 (45.26)	4.39 (3.80)	3.00 (3.10)	1905s, 1795s 1675w [h]	5.16(s), 3.74 (sept), 0.84 (d) 0.63 (d), J = 2.7 Hz; 7.15—7.76 (m)
cis-$(C_5H_5)W(CO)_2[C_2(CN)_4](\eta^1\text{-}C_6H_5CN\text{-}i\text{-}C_3H_7)$, XII	115 (dec.)	45	47.51 (47.69)	3.20 (2.96)	11.85 (12.09)	2212w, 1968s, 1878s, 1595w [h]	6.20 (s), 7.4—7.7(m), 4.68 (sept) (J = 6.7 Hz) 1.36 (d), 1.24 (d)
$(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(C_6H_4)]$, XIII	126.5 (dec)	27	69.89 (69.37)	4.61 (4.59)	4.03 (4.26)	1927s, 3333w [d]	4.87 (s), 7.13 (m), 7.84 (m) [b]
$(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$, XIV	175 (dec)	48	[f]			1920s, 3320w [d]	2.25 (s), 6.50 (s), 6.61 (m), 7.40 (m) [b]
$(C_5H_5)W(CO)_2[C(C_6H_5)N(H)(C_6H_4)]$, XV	174 (dec)	24	48.98 (49.51)	3.23 (3.12)	2.77 (2.89)	1949s, 1874s 3327w [d]	4.67 (s), 7.07 (m) [c]

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[a] THF. [b] Acetone-d_6. [c] Hexanes. [d] $CDCl_3$. [e] Contains one H_2O of crystallization. [f] Analysis confirmed by crystal structure analysis. [g] Contains 0.5 hexane of crystallization. [h] CH_2Cl_2. [i] Toluene-d_8. [j] Major isomer. [k] Both isomers.

is bonded to both metal atoms and could be described as a bridging carbenoid carbon. The distances Co(1)—C(6) and Co(2)—C(6) are 2.053(6) Å and 1.980(6) Å respectively, and compare favorably with the cobalt—carbon distances 2.05(2) Å and 1.99(2) Å found in the complex $Co_2(CO)_7(CHCHCOCO)$ where a γ-lactone ring which bridges two cobalt atoms has also been described as a carbene [16]. Atoms N(2) and C(5) are not involved in coordination to the metal atoms.

A similar bis-imidoyl carbenoid chelating ligand bonded to a single metal atom was structurally characterized in the complex $Cl_3(CO)Rh[C(C_6H_5)N(CH_3)\text{-}C(C_6H_5)N(CH_3)]$ which was formed in the reaction of $[Rh(CO)_2Cl]_2$ with $C_5H_5\text{-}(Cl)CNCH_3$ [8].

The compound $Co_2(CO)_5(C_8H_{12})_2$, formed by the reaction of cobalt carbonyl and two molecules of cyclooctyne is structurally related but has subtle structural differences [17]. In this compound two acetylenic units have fused and united with the dicobalt nucleus to form a five membered metallacyclic ring in which the four carbon atoms are π-bonded to the second cobalt atom. In our compound the π-bonding network of the $[C_6H_5CNC_6H_5]_2$ unit which could be visualized as the partial dimerization of two diphenylnitrilium ions does not directly bond to the second cobalt atom.

$(\eta^5\text{-}C_5H_5)Fe(CO)[(C_6H_5)CNH(C_6H_3CH_3)]$, XIV

The molecular structure of XIV is shown in Fig. 2. The coordination around the iron atom includes a regular η^5-cyclopentadienyl ring, a linear carbonyl group, and a phenyl-*N*-*p*-tolylamino carbene ligand in which the tolyl ring is also bonded to the iron atom at an *ortho* position. This leads to the formation of a five-membered metallacyclic ring which includes the atoms Fe, C(2), N,

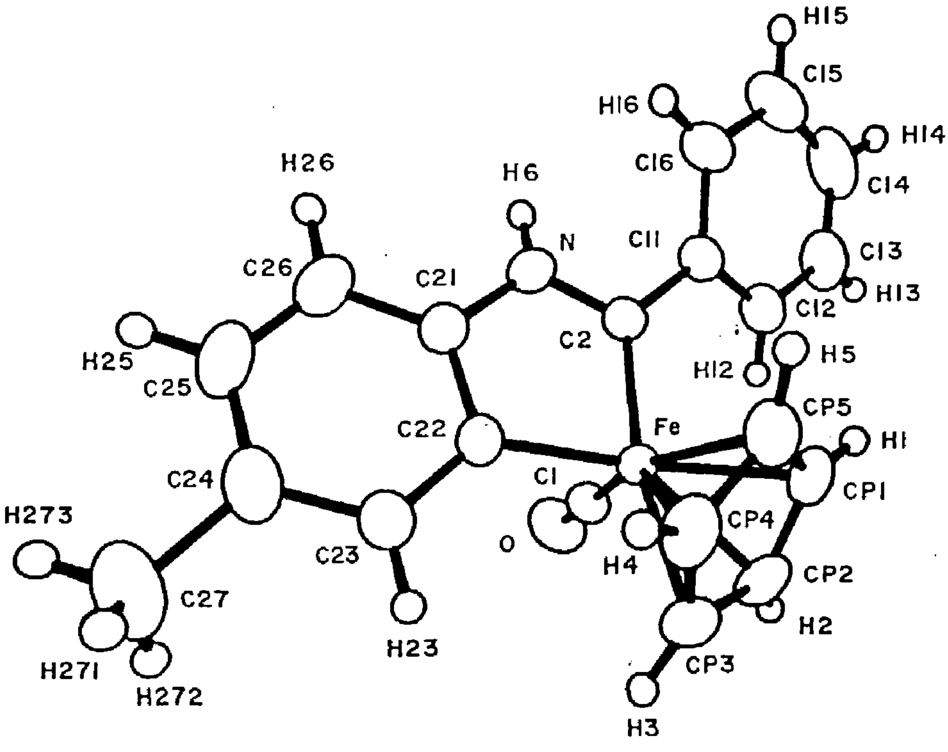

Fig. 2. An ORTEP diagram of $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$ showing 50% probability ellipsoids for all non-hydrogen atoms.

C(21) and C(22). In this respect it is quite similar to the complex $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)[C{=}NC_6H_{11}(CNHC_6H_{11})CH\{CNHC(CH_3)_3\}]$, XVI, which also contains an aminocarbene ligand in a five-membered metallacyclic ring [18]. Our iron—carbene distance, Fe—C(2) of 1.916(2) Å is similar to the corresponding distance of 1.932(3) Å found in complex XVI. However, both these distances are significantly shorter than the iron—carbene distance of 2.007(5) Å found in the diaminocarbene complex $Fe(CO)_4(\overline{CNCH_3CHCHN}CH_3)$ [19], which does not contain a metallacyclic ring. The C(2)—N distance of 1.326(2) Å is typical of aminocarbenes and compares favorably with the corresponding distance 1.336(3) Å found in XVI. Table 1 lists least squares planes of pertinent atomic groupings. The carbene ligand defined by the atoms C(11), C(2), N, and C(21) (plane 4). is planar and also contains the iron atom. The carbene ligand and the *ortho*-metallated ring (plane 3) are essentially coplanar with the dihedral angle being only 1.9°. The phenyl ring (plane 2) is twisted 21.5° from the plane of the carbene.

All hydrogen atoms were located and refined and all sixteen C—H distances lie in the range 0.88—0.96 Å. As expected, the N—H distance is significantly shorter (0.82(2) Å).

Experimental

General

All reactions were performed under a nitrogen atmosphere using standard Schlenk glassware. The solvents THF, toluene, and hexanes were dried by refluxing over sodium benzophenone and distilled under nitrogen just prior to use. $[(C_5H_5)Ni(CO)]_2$, $Co_2(CO)_8$ and $[(C_5H_5)Fe(CO)_2]_2$ were purchased from Strem Chemicals Inc., Newburyport, Mass. The reagents $C_6H_5(Cl)CNC_6H_5$, $C_6H_5(Cl)CN(p\text{-}C_6H_4CH_3)$, $C_6H_5(Cl)CN(i\text{-}C_3H_7)$, $Na[(C_5H_5)W(CO)_3]$, $Na[(C_5H_5)\text{-}Fe(CO)_2]$, $Na[Co(CO)_4]$ and $K[(C_5H_5)Ni(CO)]$ were prepared by standard methods [20,21].

All infrared spectra were recorded on a Perkin—Elmer 237 infrared spectrometer and were calibrated with polystyrene at 1601.4 cm^{-1}. NMR spectra were recorded on a Perkin—Elmer R-32 spectrometer or the Southern New England High Field NMR facility operating at 270 MHz for ^{1}H nuclei and were calibrated with TMS. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

Preparations

$(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_5CNC_6H_5)$, I. 1.82 g (8.48 mmol) of $C_6H_5(Cl)CNC_6H_5$ was added to a flask containing $Na[C_5H_5Fe(CO)_2]$ (prepared in situ by Na(Hg) reduction of 1.5 g (4.24 mmol) of $[C_5H_5Fe(CO)_2]_2$) in 100 ml THF at −78°C. The reaction flask was then allowed to warm to room temperature and stirred for $1\frac{1}{4}$ h. The solvent was removed in vacuo. The residue was taken up in benzene and chromatographed on $Al_2O_3 \cdot 6\%\ H_2O$. After elution small amounts of impurities $[C_5H_5Fe(CO)_2]_2$ and $[(C_5H_5)Fe(CO)_2]_2Hg$, a large pale yellow band of $(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_6H_5CNC_6H_5)$ was eluted with C_6H_6/THF (1/1) solvent. The product was recrystallized from toluene/hexane solution by cooling to −20°C. Other products, II—VI, were prepared and isolated similarly. Typical yields are given in Table 1.

$Co_2(CO)_6[C_6H_5CNC_6H_5]_2$, VIII. 1.89 g (8.77 mmol) $C_6H_5(Cl)CN(C_6H_5)$ was added to a solution of $NaCo(CO)_4$, prepared from 1.5 g (4.38 mmol) of $Co_2(CO)_8$) in 100 ml THF at room temperature. After 48 h, the solvent was removed. The residue was taken up in C_6H_6 and chromatographed on florisil with benzene. An orange band of product was eluted and the solvent removed in vacuo. The residue was extracted with hexanes and filtered. The solution was concentrated and crystals formed when it was cooled to −20°C.

$Co_2(CO)_5(P(CH_3)_2(C_6H_5))[C_6H_5CNC_6H_5]_2$, IX. 0.29 g (0.45 mmol) of $Co_2(CO)_6[(C_6H_5)CN(C_6H_5)]_2$ was dissolved in 90 ml of THF solvent. At −78°C 0.064 ml (0.45 mmol) of $P(CH_3)_2(C_6H_5)$ was added via syringe. Over the course of 1 h the solution changed color from orange to red. The solution was concentrated and chromatographed over $Al_2O_3 \cdot 6\%\ H_2O$ with benzene solvent. The product eluted as a red band. It was crystallized from hexane solvent when cooled to −20°C.

$(C_5H_5)Fe(CO)(CN\text{-}i\text{-}C_3H_7)(C_6H_5)$, X. 0.35 g of $(C_5H_5)Fe(CO)_2[(C_6H_5)CN(i\text{-}C_3H_7)]$ was dissolved in 50 ml THF. The solution was irradiated externally with UV iradition for 1 h. The solution was concentrated and quickly eluted over a 4″ column of alumina with THF. A yellow band eluted and the solvent was removed in vacuo. The residue was extracted with pentane, filtered, concentrated and crystallized when cooled to −20°C.

$(C_5H_5)W(CO)_2(\eta^2\text{-}C_6H_5CN\text{-}i\text{-}C_3H_7)$, XI. 0.48 g of VI was dissolved in 50 ml THF and photolyzed for $1\frac{1}{2}$ h. The solution turned brown and the solvent was removed in vacuo. The oily residue was taken up in benzene and chromatographed over $Al_2O_3 \cdot 6\%\ H_2O$ with C_6H_6. A brown band was eluted and collected. The product was recrystallized from toluene/hexane (1/5 v/v) at −20°C.

$(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$, XIV. 0.5 g of $(C_5H_5)Fe(CO)_2[(C_6H_5)CN(p\text{-}CH_3C_6H_4)]$ was dissolved in 100 ml of hexane and irradiated externally for $1\frac{1}{4}$ h. The solvent was removed in vacuo. The residue was taken up in benzene and chromatographed over $Al_2O_3 \cdot 5\%\ H_2O$ with benzene solvent. The product, as a red band, was collected and crystallized from hexane solvent by cooling to −20°C. The compounds $(C_5H_5)Fe(CO)[(C_6H_5)CN(H)(C_6H_4)]$ and $C_5H_5W(CO)_2[(C_6H_5)CN(H)(C_6H_4)]$ were prepared similarly.

Structure determination

General

All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer. Unit cells were determined and refined using 25 randomly selected reflections obtained with the CAD-4 automatic search, center, index, and least squares routines. Space groups were determined from the systematic absences observed during data collection.

All calculations were performed on a Digital PDP-11/45 computer using the Enraf-Nonius SDP program library. Both structures were solved by the heavy atom method. Anomalous dispersion corrections [22a] were made for scattering [22b] by all nonhydrogen atoms. Full matrix least squares refinements minimized the function $\sum_{hkl} w(F_{obs} - F_{calc})^2$ where the weighting factor w =

(Continued on p. 263)

TABLE 2

CRYSTALLOGRAPHIC DATA FOR THE STRUCTURES $Co_2(CO)_5(P(CH_3)_2(C_6H_5))[(C_6H_5)CN(C_6H_5)]_2$, IX AND $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3\text{-}C_6\text{-}H_3)]$, XIV

	IX	XIV
(A) Crystal parameters at 23°C		
Formula	$C_{39}H_{31}N_2O_5PCo_2$	$C_{20}H_{17}NOFe$
Space group	$P2_1/n$	$P2_1/c$
a	12.185(4) Å	16.296(3) Å
b	15.749(5) Å	9.756(1) Å
c	18.874(6) Å	10.613(2) Å
β	95.49(3)°	107.35(16)°
V	3505	1610(1) Å^3
Z	4	4
ρ_{calc}	1.39 g/cm^3	1.42 g/cm^3
M. Wt.	756.52	343.22
(B) Measurements of intensity data		
Radiation	Mo-K_α	Mo-K_α
Monochromator	Graphite	Graphite
Detector aperture:		
Horizontal =	A = 2.5 mm	A = 3.0 mm
$A + B \tan\theta$	B = 1.0 mm	B = 1.0 mm
Vertical	4 mm	4 mm
Crystal detector distance	330 mm	330 mm
Reflections measured	$+h, +k, \pm l$	$+h, +k, \pm l$
Max. 2θ	50°	56°
Scan type	coupled θ (crystal) — 2 θ (counter)	coupled θ (crystal) — 2 θ (counter)
θ Scan width	0.85° + 0.35 tan θ	0.65° + 0.35 tan θ
Background:	1/4 additional scan at each end of scan	1/4 additional scan at each end of scan
θ Scan rate Max	6.67°/min	10.0°/min
Min	1.33°/min	1.1°/min
No reflections measured	6900	4169
Data used: $(F^2 > 3.0\sigma(F^2))$	2524	2517
(C) Treatment of data		
Absorption coeff., μ	10.43	9.75
Grid	—	8 X 8 X 10
Transmission factors		
Max.		0.887
Min.		0.537
Ignorance factor, p	0.04	0.04
(D) Solution and refinement data		
R	0.061	0.028
R_w	0.068	0.037
Shift/error—final cycle		
Max: (Nonhydrogen)	0.05	0.62
Hydrogen atoms	calculated (not refined)	refined
Final diff. Fourier peak max. $e^-/Å^3$	0.568	0.332
Error obs. of unit wt.	1.71	1.56

TABLE 3

POSITIONAL PARAMETERS FOR $Co_2(CO)_5(P(CH_3)_2C_6H_5)[(C_6H_5)CN(C_6H_5)]_2$ WITH ESD's

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)	0.3199(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(6)
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(5)	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)

TABLE 4

BOND DISTANCEZ WITH ESD's FOR $Co_2(CO)_5(P(CH_3)_2C_6H_5)[C_6H_5CNC_6H_5]_2$

Atoms	Distance (Å)	Atoms	Distance (Å)
Co(1)—Co(2)	2.447(1)	C(24)—C(25)	1.332(11)
Co(1)—P	2.229(2)	C(25)—C(26)	1.401(11)
Co(1)—C(1)	1.912(7)	C(26)—C(21)	1.355(9)
Co(1)—C(2)	1.758(8)	N(2)—C(31)	1.452(8)
Co(1)—C(7)	1.737(8)	C(31)—C(32)	1.370(9)
Co(1)—C(6)	2.053(6)	C(32)—C(33)	1.408(10)
Co(2)—C(6)	1.980(6)	C(33)—C(34)	1.340(10)
Co(2)—C(1)	1.897(7)	C(34)—C(35)	1.360(10)
Co(2)—C(4)	1.768(8)	C(35)—C(36)	1.387(10)
Co(2)—C(3)	1.715(8)	C(36)—C(31)	1.399(9)
Co(2)—N(1)	2.008(5)	C(6)—C(41)	1.500(9)
P—C(57)	1.828(9)	C(41)—C(42)	1.409(9)
P—C(58)	1.817(8)	C(42)—C(43)	1.385(10)
P—C(51)	1.806(8)	C(43)—C(44)	1.366(10)
C(6)—N(2)	1.468(8)	C(44)—C(45)	1.363(10)
N(2)—C(5)	1.363(7)	C(45)—C(46)	1.404(10)
C(5)—N(1)	1.311(7)	C(46)—C(41)	1.404(9)
N(1)—C(11)	1.453(8)	C(51)—C(52)	1.364(11)
C(11)—C(12)	1.372(9)	C(52)—C(53)	1.457(14)
C(12)—C(13)	1.434(11)	C(53)—C(54)	1.343(13)
C(13)—C(14)	1.289(11)	C(54)—C(55)	1.322(13)
C(14)—C(15)	1.341(11)	C(55)—C(56)	1.380(12)
C(15)—C(16)	1.424(10)	C(56)—C(51)	1.382(10)
C(16)—C(11)	1.361(9)	C(1)—O(1)	1.192(7)
C(5)—C(21)	1.481(9)	C(2)—O(2)	1.158(7)
C(21)—C(22)	1.396(9)	C(3)—O(3)	1.182(8)
C(22)—C(23)	1.401(10)	C(4)—O(4)	1.167(8)
C(23)—C(24)	1.355(11)	C(7)—O(7)	1.161(8)

$1/\sigma(F)^2$. Unweighted and weighted discrepancy indices were determined by the formulae:

$$R = \frac{\Sigma \| F_{\text{obs}}| - |F_{\text{calc}}\|}{\Sigma |F_{\text{obs}}|}$$

$$R_w = \left[\frac{\Sigma w |F_{\text{obs}} - F_{\text{calc}}|^2}{\Sigma w |F_{\text{obs}}|^2} \right]^{1/2}$$

Crystal data, data collection parameters, structure solution and refinement data for the individual structures are presented in Table 2. Tables 3—5 list various structural results for $Co_2(CO)_5(P(CH_3)_2C_6H_5)[C_6H_5CNC_6H_5]_2$, IX. Tables 6—8 list structural results for $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$, XIV. Tables of thermal parameters, least squares planes, hydrogen atom positions for the structure of IX, and structure factor amplitudes for both structures are available *.

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TABLE 5

INTERATOMIC ANGLES WITH ESD's FOR $Co_2(CO)_5(P(CH_3)_2C_6H_5)[C_6H_5CNC_6H_5]_2$

Atoms	Angle (°)	Atoms	Angle (°)
C(2)—Co(1)—C(7)	108.3(3)	C(1)—Co(2)—C(6)	83.5(3)
C(2)—Co(1)—P	92.3(2)	C(1)—Co(2)—Co(1)	50.3(2)
C(2)—Co(1)—Co(2)	98.8(2)	C(6)—Co(2)—Co(1)	54.0(2)
C(2)—Co(1)—C(1)	142.9(3)	Co(1)—C(1)—O(1)	142.2(6)
C(2)—Co(1)—C(6)	93.4(3)	Co(2)—C(1)—O(1)	137.9(6)
C(7)—Co(1)—C(1)	108.8(3)	Cp(1)—C(1)—Co(2)	79.9(3)
C(7)—Co(1)—C(6)	98.0(3)	Co(1)—C(2)—O(2)	176.9(7)
C(7)—Co(1)—P	93.1(2)	Co(2)—C(7)—O(7)	175.7(7)
C(7)—Co(1)—Co(2)	140.5(2)	Co(2)—C(3)—O(3)	175.8(7)
C(1)—Co(1)—Co(2)	49.8(2)	Co(2)—C(4)—O(4)	176.2(7)
C(1)—Co(1)—P	86.1(2)	Co(2)—C(6)—Co(1)	74.7(2)
C(1)—Co(1)—C(6)	81.2(3)	Co(2)—C(6)—C(41)	115.7(4)
C(6)—Co(1)—Co(2)	51.3(2)	Co(1)—C(6)—C(41)	122.5(5)
C(6)—Co(1)—P	165.3(2)	N(2)—C(6)—C(41)	110.9(5)
P—Co(1)—Co(2)	114.33(6)	Co(2)—C(6)—N(2)	109.1(4)
C(3)—Co(2)—C(4)	96.0(4)	Co(1)—C(6)—N(2)	118.2(4)
C(3)—Co(2)—N(1)	109.1(3)	Co(1)—P—C(57)	112.8(3)
C(3)—Co(2)—C(1)	100.0(3)	Co(1)—P—C(58)	114.3(3)
C(3)—Co(2)—C(6)	98.8(3)	Co(1)—P—C(51)	118.2(3)
C(3)—Co(2)—Co(1)	137.3(3)	C(57)—P—C(58)	103.3(4)
C(4)—Co(2)—C(1)	91.2(3)	C(57)—P—C(51)	103.5(4)
C(4)—Co(2)—N(1)	96.2(3)	C(58)—P—C(51)	103.3(4)
C(4)—Co(2)—C(6)	164.9(3)	P—C(51)—C(52)	120.5(7)
C(4)—Co(2)—Co(1)	112.2(3)	P—C(51)—C(56)	122.0(7)
N(1)—Co(2)—C(1)	149.9(3)	C(56)—C(51)—C(52)	117.3(8)
N(1)—Co(2)—C(6)	81.6(2)	C(51)—C(52)—C(53)	119.7(10)
N(1)—Co(2)—Co(1)	99.3(2)	C(52)—C(53)—C(54)	117.4(11)
C(6)—C(41)—C(42)	119.0(6)	C(53)—C(54)—C(55)	124.6(12)
C(6)—C(41)—C(46)	123.5(6)	C(54)—C(55)—C(56)	117.2(11)
C(46)—C(41)—C(42)	117.1(7)	C(55)—C(56)—C(51)	123.6(9)
C(41)—C(42)—C(43)	121.2(7)	N(1)—C(11)—C(12)	119.2(6)
C(42)—C(43)—C(44)	121.1(8)	N(1)—C(11)—C(16)	119.9(6)
C(43)—C(44)—C(45)	121.1(8)	C(11)—C(12)—C(13)	117.1(7)
C(44)—C(45)—C(46)	119.8(8)	C(12)—C(13)—C(14)	120.4(9)
C(45)—C(46)—C(41)	120.7(7)	C(13)—C(14)—C(15)	124.7(9)
C(31)—N(2)—C(5)	121.0(5)	C(14)—C(15)—C(16)	116.8(8)
C(6)—N(2)—C(5)	117.6(5)	C(15)—C(16)—C(11)	120.1(7)
C(6)—N(2)—C(31)	120.8(5)	C(16)—C(11)—C(12)	120.9(7)
N(2)—C(31)—C(32)	123.0(6)		
N(2)—C(31)—C(36)	117.8(6)		
C(31)—C(32)—C(33)	119.5(7)		
C(32)—C(33)—C(34)	120.6(8)[		
C(33)—C(34)—C(35)	121.0(8)		
C(34)—C(35)—C(36)	119.9(7)		
C(35)—C(36)—C(31)	119.9(7)		
C(36)—C(31)—C(32)	119.1(7)		
N(2)—C(5)—C(21)	121.7(6)		
N(2)—C(5)—N(1)	115.2(6)		
N(1)—C(5)—C(21)	123.1(6)		
C(5)—C(21)—C(22)	117.6(6)		
C(5)—C(21)—C(26)	123.0(7)		
C(26)—C(21)—C(22)	119.1(7)		
C(21)—C(22)—C(23)	119.6(7)		
C(22)—C(23)—C(24)	118.3(9)		
C(23)—C(24)—C(25)	123.4(9)		
C(24)—C(25)—C(26)	118.4(9)		
C(25)—C(26)—C(21)	121.0(8)		
C(11)—N(1)—C(5)	119.9(6)		
Co(2)—N(1)—C(5)	115.8(4)		
Co(2)—N(1)—C(11)	124.1(4)		

TABLE 6

FINAL ATOMIC POSITIONAL PARAMETERS WITH ESD's FOR $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Fe	0.24232(2)	0.03002(1)	0.09838(3)	C(25)	0.1371(2)	−0.4295(2)	0.0646(3)
O	0.3690(1)	−0.0581(2)	0.3388(2)	C(26)	0.1962(2)	−0.3852(2)	0.0035(1)
N	0.2826(1)	−0.1892(2)	−0.0368(2)	C(27)	0.0405(2)	−0.3877(3)	0.2092(3)
Cp(1)	0.2360(1)	0.2355(2)	0.0303(2)	H(1)	0.278(1)	0.279(3)	0.005(2)
Cp(2)	0.2304(1)	0.2325(2)	0.1597(2)	H(2)	0.268(1)	0.268(3)	0.229(2)
Cp(3)	0.1564(1)	0.1558(2)	0.1602(2)	H(3)	0.140(2)	0.132(3)	0.232(2)
Cp(4)	0.1170(1)	0.1116(2)	0.0295(2)	H(4)	0.069(2)	0.063(3)	−0.002(2)
Cp(5)	0.1660(2)	0.1592(2)	−0.0508(2)	H(5)	0.155(2)	0.140(3)	−0.140(2)
C(1)	0.3202(1)	−0.0197(2)	0.2420(2)	H(12)	0.411(2)	0.146(3)	0.063(2)
C(2)	0.2997(1)	−0.0571(2)	−0.0136(2)	H(13)	0.498(1)	0.248(3)	−0.048(2)
C(11)	0.3581(1)	0.0059(2)	−0.0815(2)	H(14)	0.500(2)	0.184(3)	−0.248(2)
C(12)	0.4108(1)	0.1161(2)	−0.0229(2)	H(15)	0.415(2)	−0.005(3)	−0.348(3)
C(13)	0.4635(1)	0.1791(3)	−0.0866(3)	H(16)	0.323(2)	−0.108(3)	−0.249(2)
C(14)	0.4653(2)	0.1350(3)	−0.2083(3)	H(23)	0.112(2)	−0.144(3)	0.210(2)
C(15)	0.4141(2)	0.0252(3)	−0.2683(2)	H(25)	0.121(2)	−0.518(3)	0.055(2)
C(16)	0.3606(1)	−0.0395(3)	−0.2059(2)	H(26)	0.219(2)	−0.443(2)	−0.051(2)
C(21)	0.2229(2)	−0.2484(2)	0.0199(2)	H(6)	0.309(1)	−0.324(3)	−0.077(2)
C(22)	0.1924(1)	−0.1540(2)	0.0954(2)	H(271)	−0.014(2)	−0.350(3)	0.170(2)
C(23)	0.1328(1)	−0.2043(2)	0.1554(2)	H(272)	0.060(2)	−0.369(3)	0.302(2)
C(24)	0.1045(1)	−0.3405(2)	0.1409(2)	H(273)	0.034(2)	−0.479(3)	0.205(2)

TABLE 7

BOND DISTANCES WITH ESD's FOR $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$

Atoms	Distance (Å)	Atoms	Distance (Å)
Fe—Cp(1)	2.123(2)	C(23)—C(24)	1.400(3)
Fe—Cp(2)	2.107(2)	C(24)—C(25)	1.397(3)
Fe—Cp(3)	2.108(2)	C(25)—C(26)	1.380(3)
Fe—Cp(4)	2.108(2)	C(26)—C(21)	1.398(3)
Fe—Cp(5)	2.113(2)	C(24)—C(27)	1.508(3)
Fe—C(1)	1.736(2)	Cp(1)—Cp(2)	0.91(2)
Fe—C(2)	1.916(2)	Cp(2)—Cp(3)	0.87(2)
Fe—C(22)	1.968(2)	Cp(3)—Cp(4)	0.91(2)
Cp(1)—H(1)	1.404(3)	Cp(4)—Cp(5)	0.89(2)
Cp(2)—H(2)	1.421(3)	Cp(5)—Cp(1)	0.93(2)
Cp(3)—H(3)	1.411(3)	C(12)—H(12)	0.95(2)
Cp(4)—H(4)	1.409(3)	C(13)—H(13)	0.89(2)
Cp(5)—H(5)	1.417(3)	C(14)—H(14)	0.93(2)
C(1)—O	1.158(2)	C(15)—H(15)	0.90(3)
C(2)—N	1.326(2)	C(16)—H(16)	0.93(3)
C(2)—C(11)	1.488(2)	C(23)—H(23)	0.96(2)
C(11)—C(12)	1.400(3)	C(25)—H(25)	0.90(2)
C(12)—C(13)	1.386(3)	C(26)—H(26)	0.96(2)
C(13)—C(14)	1.370(4)	C(27)—H(271)	0.94(3)
C(14)—C(15)	1.390(4)	C(27)—H(272)	0.96(3)
C(15)—C(16)	1.394(3)	C(27)—H(273)	0.89(2)
C(16)—C(11)	1.404(3)	N—H(6)	0.82(2)
N—C(21)	1.411(2)		
C(21)—C(22)	1.406(2)		
C(22)—C(23)	1.399(2)		

TABLE 8

SELECTED BOND ANGLES WITH ESD's FOR $(C_5H_5)Fe(CO)[C(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$

Atoms	Angle (°)	Atoms	Angle (°)
Cp(5)—Cp(1)—Cp(2)	108.0(2)	C(12)—C(13)—C(14)	120.7(2)
Cp(1)—Cp(2)—Cp(3)	108.4(2)	C(13)—C(14)—C(15)	119.7(2)
Cp(2)—Cp(3)—Cp(4)	107.2(2)	C(14)—C(15)—C(16)	120.4(2)
Cp(3)—Cp(4)—Cp(5)	108.6(2)	C(15)—C(16)—C(11)	120.1(2)
Cp(4)—Cp(5)—Cp(1)	107.7(2)	C(2)—N—C(21)	116.9(1)
Cp(1)—Fe—Cp(2)	38.8(1)	C(2)—N—H(6)	121(2)
Cp(1)—Fe—Cp(5)	39.1(1)	C(21)—N—H(6)	122(2)
Cp(2)—Fe—Cp(3)	39.4(1)	N—C(21)—C(22)	112.4(1)
Cp(3)—Fe—Cp(4)	39.1(1)	N—C(21)—C(26)	124.5(2)
Cp(4)—Fe—Cp(5)	39.0(1)	C(26)—C(21)—C(22)	123.1(2)
C(1)—Fe—C(2)	93.2(1)	C(21)—C(22)—C(23)	116.2(2)
C(1)—Fe—C(22)	87.1(1)	C(22)—C(23)—C(24)	122.2(2)
C(2)—Fe—C(22)	82.0(1)	C(23)—C(24)—C(25)	118.9(2)
N—C(2)—C(11)	116.2(1)	C(24)—C(25)—C(26)	121.1(2)
Fe—C(2)—C(11)	128.2(1)	C(25)—C(26)—C(21)	118.4(2)
Fe—C(2)—N	115.6(1)	C(23)—C(24)—C(27)	119.3(2)
C(2)—C(11)—C(12)	119.8(2)	C(25)—C(24)—C(27)	121.8(2)
C(2)—C(11)—C(16)	121.8(2)	Fe—C(1)—O	176.4(2)
C(11)—C(12)—C(13)	120.7(2)	Fe—C(22)—C(21)	113.1(1)
		Fe—C(22)—C(23)	130.7(1)

$Co_2(CO)_5(P(CH_3)_2C_6H_5)[C_6H_5CNC_6H_5]_2$

In the early stages of refinement all atoms in the bis-imidoyl ligand were refined as carbon atoms. Two atoms showed unusually small temperature factors and were reassigned as the nitrogen atoms. Hydrogen atom positions were calculated using idealized geometry. Their contributions were included in structure factor calculations, but their positions were not refined.

$(C_5H_5)Fe(CO)[(C_6H_5)N(H)(p\text{-}CH_3C_6H_3)]$

Hydrogen atom positions were obtained from difference Fourier maps. Only their positional parameters were refined.

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