Arenediazonium Complexes of Cobalt(I): Synthesis and Properties[†]

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Arenediazonium complexes of cobalt(I) of the type $[Co(RN_2)L_4][BPh_4]_2$ [L = $P(OEt)_2Ph$, $P(OEt)_3$, or $P(OMe)_3$; R = $4\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $2\text{-}CH_3C_6H_4$, C_6H_5, $4\text{-}CH_3OC_6H_4$, $4\text{-}ClC_6H_4$, or $4\text{-}FC_6H_4$] have been prepared; their characterization by i.r., ^1H, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra is reported. Reactivity with π-acceptor ligands such as CO, NO, isocyanide, and phosphite is also described. Finally, the reaction of the arenediazonium complexes with chloride ions affording the cobalt(II) derivatives $[CoClL_4]^+$ has been investigated; the function of RN_2 as an oxidizing agent in this reaction is also discussed.

The chemistry of the aryldiazenido and aryldiazene complexes has been an area of intense interest in recent years,[1,2] not only because of the close relationship of arenediazonium (RN_2^+) with nitrosyl and dinitrogen ligands but also because of the varied modes of bonding of these ligands and their utility as intermediates in the synthesis of aryldiazene and arylhydrazine derivatives. Although a large number of studies on synthesis, structure, bonding, and reactivity of aryldiazenido complexes of several metals have been carried out,[1-3] very few have been concerned with the cobalt atom. Except for the work of Lalor and co-workers[4] on the unstable Co^{1-} compound $[Co(C_6H_5N_2)(CO)_2(PPh_3)]$, no other data are available on the aryldiazenido cobalt complexes. We previously reported[5] on the chemistry of nitrosyl cobalt complexes with phosphite ligands and, as an extension of our studies, we now describe the synthesis, characterization, and reactivity of the first example of arenediazonium derivatives of cobalt(I).

Experimental

Materials.—All the solvents used were purified and dried by standard methods and distilled under a stream of nitrogen just prior to use. Anhydrous CoI_2 was an Alfa Inorganic Ventron chemical product and was used as received. Diethoxy(phenyl)phosphine was prepared by the method of Rabinowitz and Pellon;[6] triethyl phosphite and trimethyl phosphite were Baker chemical products and were purified by distillation under nitrogen. Diazonium salts were prepared in the usual way as described in the literature.[7] 4-Tolyl isocyanide was obtained by the phosgene method of Ugi *et al.*[8] All other reagents were used as received.

Synthesis of the Complexes.—All preparations and reactions were carried out under pure, dry dinitrogen using standard Schlenk techniques. Once isolated, the complexes were found to be stable in air for 1—2 d.

$[Co(CO)L_4]BPh_4$ [L = $P(OEt)_2Ph$, $P(OEt)_3$, *or* $P(OMe)_3$]. These complexes were prepared by a modification of the method reported for synthesis of the diethoxy(phenyl)phosphine derivative.[9] The appropriate phosphite was added to a solution of anhydrous CoI_2 (3.13 g, 10 mmol) in ethanol or methanol (60 cm^3). The reaction mixture was stirred for 30 min and then allowed to stand under carbon monoxide for 1—2 h, until the solution turned orange. After filtration, the addition of $NaBPh_4$ (1.7 g, 5 mmol) afforded a yellow precipitate which was filtered off and crystallized from ethanol or methanol; yield $\geqslant$ 45% {Found [L = $P(OEt)_2Ph$]: C, 65.25; H, 6.70. Calc. for $C_{65}H_{80}BCoO_9P_4$: C, 65.1; H, 6.75%}; $\nu(CO)$ (CH_2Cl_2) 2 005vw, 1 956s cm^{-1} {Found [L = $P(OEt)_3$]: C, 55.15; H, 7.60. $C_{49}H_{80}BCoO_{13}P_4$ requires C, 54.95; H, 7.55%}; m.p. 120 °C; Λ_M 54.7 S cm^2 mol^{-1}; $\nu(CO)$ (CH_2Cl_2) 2 010vw, 1 958s cm^{-1}; δ(H) $[(CD_3)_2CO]$ 7.35 (br), 6.88 (m) (20 H, 4 C_6H_5); 4.15 m (24 H, 12 CH_2), 1.31 (t, 36 H, 12 CH_3) {Found [L = $P(OMe)_3$]: C, 49.3; H, 6.35. $C_{37}H_{56}BCoO_{13}P_4$ requires C, 49.25; H, 6.25%}; m.p. 154 °C; Λ_M 61.5 S cm^2 mol^{-1}; $\nu(CO)$ (CH_2Cl_2) 2 115vw, 1 973s cm^{-1}; δ(H) $[(CD_3)_2CO]$ 7.33 (m), 6.88 (m) (20 H, 4 C_6H_5); 3.72 (d, 36 H, 12 CH_3).

$[Co(RN_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$ (R = $4\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $2\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, C_6H_5, $4\text{-}ClC_6H_4$, *or* $4\text{-}FC_6H_4$). An excess of the appropriate diazonium salt, $[RN_2]BF_4$ (3 mmol), was added at room temperature to a solution of $[Co(CO)\{P(OEt)_2Ph\}_4]BPh_4$ (1.2 g, 1 mmol) in dichloromethane (80 cm^3). Nitrogen was bubbled through the reaction mixture to remove the carbon monoxide formed during the reaction. After 50—80 min the unreacted diazonium salt was separated by filtration and the resulting solution evaporated to dryness. The green oil obtained was triturated with ethanol (20 cm^3) and $NaBPh_4$ (0.34 g, 1 mmol) was added to give a green product which was crystallized from dichloromethane–ethanol (1:10); yield $\geqslant$ 65%.

$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4][BPh_4]_2$. The compound was prepared following the method reported above, starting from $[Co(CO)\{P(OEt)_3\}_4]BPh_4$ in dichloromethane and using a reaction time of 2 h; yield $\geqslant$ 75%.

$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OMe)_3\}_4][BPh_4]_2$. To a solution of $[Co\{P(OMe)_3\}_5]BPh_4$[5c] (1 g, 1 mmol) in dichloromethane (30 cm^3) an excess of 4-toluenediazonium tetrafluoroborate (0.62 g, 3 mmol) was added and the reaction mixture was stirred for 1 h. After the unreacted diazonium salt had been removed by filtration, the solvent was evaporated to dryness to give an oily product which was triturated with methanol. The addition of $NaBPh_4$ afforded a green solid which was crystallized from dichloromethane–methanol (1:10); yield $\geqslant$ 40%.

$[CoClL_4]BPh_4$ [L = $P(OEt)_2Ph$ *or* $P(OEt)_3$]. To a solution of $[Co(RN_2)L_4][BPh_4]_2$ (1 mmol) in acetone (30 cm^3) was added LiCl (3 mmol) in ethanol (10 cm^3). The reaction mixture was stirred for 2 h and the solvent then removed under reduced pressure, leaving an oil which was triturated with ethanol. The product obtained was filtered and crystallized from dichloromethane–ethanol (1:20); yield $\geqslant$ 80% {Found [L = $P(OEt)_2Ph$]: C, 63.55; H, 6.75; Cl, 3.00. Calc. for $C_{64}H_{80}BClCoO_8P_4$: C, 63.7; H, 6.70; Cl, 2.95%}; m.p. 93 °C; Λ_M 63.6 S cm^2 mol^{-1}; $\mu_{eff.}$ = 2.30 ($ClCH_2CH_2Cl$), 2.18 (solid); $\lambda_{max.}$ ($ClCH_2CH_2Cl$) 592 nm (ε 570 dm^3 mol^{-1} cm^{-1}), 657 (485), 760 (sh) {Found [L = $P(OEt)_3$]: C, 53.3; H, 7.55; Cl, 3.10. $C_{48}H_{80}BClCoO_{12}P_4$

[†] *Non-S.I. unit employed*: atm = 101 325 N m^{-2}.

requires C, 53.45; H, 7.50; Cl, 3.30%); m.p. 92 °C; Λ_M 59.1 S cm^2 mol^{-1}; $\mu_{eff.}$ = 2.10 ($ClCH_2CH_2Cl$), 2.13 (solid); $\lambda_{max.}$ ($ClCH_2CH_2Cl$) 564 (ε 255 dm^3 mol^{-1} cm^{-1}), 628 (227).

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Solid-state spectra were obtained from KBr pellets or Nujol mulls; solution spectra were obtained using potassium bromide cells. Solution ^1H n.m.r. spectra were obtained with a Varian EM-390 or Varian FT-80A spectrometer using $SiMe_4$ as an internal standard. Fourier-mode, proton-noise-decoupled ^{31}P n.m.r. spectra were collected on a Varian FT-80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, downfield shifts being considered positive. Electronic spectra were recorded on a Cary 219 spectrophotometer. Conductivities of 10^{-3} mol dm^{-3} solutions of complexes in nitromethane at 25 °C were measured with a Halosis bridge. Magnetic susceptibility measurements were performed on powdered samples at ambient temperature with a Cahn Instrument Faraday balance, using $Hg[Co(NCS)_4]$ as standard. Solution susceptibilities were determined by the Evans method.[10] Susceptibilities were corrected for diamagnetism of the ligands from tables given by Figgis and Lewis.[11]

Results and Discussion

The monocarbonyl complexes[9] $[Co(CO)L_4]^+$ [L = $P(OEt)_2Ph$ or $P(OEt)_3$] react at room temperature in dichloromethane or acetone solution with an excess of arenediazonium salt $[RN_2]BF_4$ to give arenediazonium derivatives $[Co(RN_2)L_4][BPh_4]_2$, according to reaction (1). Owing to the

$$[Co(CO)L_4]^+ + RN_2^+ \rightleftharpoons [Co(RN_2)L_4]^{2+} + CO \quad (1)$$

equilibrium (1), an excess of $[RN_2]BF_4$ must be used to obtain good yields in the arenediazonium complexes. Furthermore, the CO must not only be removed from the solution for the back reaction, but also because a secondary reaction (2) takes place with CO, forming the known dicarbonyl complexes.[9]

$$[Co(CO)L_4]^+ + CO \longrightarrow [Co(CO)_2L_3]^+ + L \quad (2)$$

The reactivity of trimethyl phosphite derivative $[Co(CO)\{P(OMe)_3\}_4]^+$ towards the arenediazonium cation was studied in different conditions, but in every case no evidence of the formation of any arenediazonium compound was obtained, the starting carbonyl being the only isolated product. However, $[Co(4\text{-}CH_3C_6H_4N_2)\{P(OMe)_3\}_4][BPh_4]_2$ was prepared following a new method, reaction (3), which involves the displacement of a $P(OMe)_3$ ligand by the RN_2^+ group in the pentaphosphite complex.[5c]

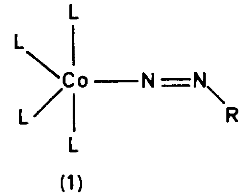
$$[Co\{P(OMe)_3\}_5]^+ + RN_2^+ \longrightarrow [Co(RN_2)\{P(OMe)_3\}_4]^{2+} + P(OMe)_3 \quad (3)$$

In an attempt to prepare arenediazonium derivatives with a different stoicheiometry, we also tested reactivity with $[RN_2]BF_4$ of other cobalt(I) complexes such as dicarbonyls[9] $[Co(CO)_2L_3]^+$ and $[CoI(CO)_2L_2]$. While the former was unreactive toward substitution with RN_2^+, the $[CoI(CO)_2L_2]$ compound quickly reacted at −30 °C in dichloromethane solution with an excess of arenediazonium cation to give a green solution, after evolution of CO. A rather unstable material was isolated from this solution, whose i.r. spectrum showed a strong ν(CO) band at 2 022 cm^{-1} and an absorption at 1 813 cm^{-1} in the ν(NN) stretching region. Unfortunately the compound was very unstable both in the solid state and in solution and decomposed on attempted recrystallization. However, on the basis of its i.r. spectrum, we tentatively assigned the formula $[CoI(RN_2)(CO)L_2]BPh_4$ to this arenediazonium compound.

Selected properties of the $[Co(RN_2)L_4]^{2+}$ complexes, which are all crystalline green solids, stable in the solid state but rather unstable in polar organic solvents, are given in Tables 1 and 2. The complexes are diamagnetic; their conductivity values (Λ_M 113.0—127.4 S cm^2 mol^{-1} in nitromethane) agree with those reported for 1:2 electrolytes containing BPh_4^- as anion.[12]

The i.r. spectra of the arenediazonium derivatives generally show the presence of two bands in the ν(NN) stretching region, both in the solid state and in CH_2Cl_2 solution (Table 1). In the case of the $[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4]^{2+}$ derivative, these two bands at 1 780 and 1 764 cm^{-1} (CH_2Cl_2 solution) shift to 1 748 and 1 729 cm^{-1} on labelling with ^{15}N (using terminally labelled arenediazonium salts, $R^{14}N{\equiv}^{15}N^+$). The presence of two or more bands was previously observed for several derivatives containing only one arenediazonium ligand and it was demonstrated that these bands result from resonance interaction of ν(NN) with the weak vibrational mode of the attached phenyl group;[2a,5] this probably applies to our derivatives. An alternative explanation, which would suggest the presence of an axial–equatorial isomerism of the RN_2^+ ligand, may not safely be rejected, although in such a case more complicated n.m.r. spectra should be obtained (Table 2). Following the method of Ibers and co-workers,[13] the values of the unperturbed ν′(NN) were calculated and these appear in Table 1. These values fall in the range 1 763—1 787 cm^{-1} and seem to indicate a single bent RNN—M arenediazonium group for the $[Co(RN_2)L_4]^{2+}$ compounds, as can be deduced by a comparison of ν(NN) with aryldiazenido complexes whose crystal structures are known, such as $[Fe(C_6H_5N_2)(CO)_2(PPh_3)_2]BF_4$,[14] $[RuCl_3(4\text{-}CH_3C_6H_4N_2)(PPh_3)_2]$,[2e,15] $[OsH(CO)(C_6H_5N_2)(PPh_3)_2]{\cdot}CH_2Cl_2$,[16] and $[Mn(CO)_2(\eta^5\text{-}C_5H_4CH_3)(2\text{-}CF_3C_6H_4N_2)]BF_4$.[1c] This assignment also agrees with the empirical roles proposed by Haymore and Ibers[15] for which the observed and corrected ν(NN) frequencies, falling above 1 530—1 540 cm^{-1}, are characteristic of a 'single bent' arenediazonium ligand.

At room temperature, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the complexes consist of a broad singlet at δ + 146.6 to + 148.5 for the $P(OEt)_2Ph$ derivatives, while two broad signals appear at δ + 128.7 and + 110.3 for the $P(OEt)_3$ compound. Lowering the sample temperature produces a complex sequence of changes in the ^{31}P spectra until, at −80 °C in [$^2H_6$]acetone, two well resolved triplets appear for all the $[Co(RN_2)L_4]^{2+}$ complexes [Figure (*a*)]. The experimental spectra can be simulated with an A_2B_2 model using the values listed in Table 2, and the good fit obtained between the observed and calculated spectra [Figure (*b*)] suggests that a trigonal-bipyramidal geometry with a 'single bent' arenediazonium group in an equatorial position can be proposed for cations $[Co(RN_2)L_4]^{2+}$, (1).



(1)

The addition of free phosphite to the solution of the complexes does not change the profile of the spectra in the temperature range −80 to +40 °C and the peak of excess $P(OEt)_3$ or $P(OEt)_2Ph$ remains sharp throughout, confirming that the exchange observed is intramolecular. For the five-coordinate d^8 phosphite complexes,[17] phosphorus exchange occurs through an intramolecular rearrangement following the

Table 1. Physical, analytical, selected i.r., and electronic absorption data for the arenediazonium complexes

Compounds	M.p./°C	Λ_M[a]/ S cm^2 mol^{-1}	Analysis[b] (%) C	H	N	ν(NN)[c]/cm^{-1}					ν'(NN)[c,d]/ cm^{-1}	Visible spectra[e] $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$[f]	122	116.0	71.25 (70.90)	6.80 (6.70)	1.80 (1.75)	1 822sh	1 780s (1 780s)		1 764s (1 770s)		1 772 (1 772)	588 (164)
$[Co(3\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	116	122.6	70.65 (70.90)	6.80 (6.70)	1.70 (1.75)	1 820sh (1 815sh)		1 772s (1 766s)		(1 745sh)	1 772 (1 766)	588 (166)
$[Co(2\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	129	115.0	70.85 (70.90)	6.65 (6.70)	1.65 (1.75)	1 788sh (1 820sh)		1 773s (1 772s)			1 773 (1 772)	588 (183)
$[Co(4\text{-}CH_3OC_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	108	116.9	70.40 (70.20)	6.50 (6.65)	1.70 (1.70)		1 778sh (1 782s)		1 763s (1 760s)	1 735sh (1 735sh)	1 770 (1 768)	583 (259)
$[Co(C_6H_5N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	117	120.8	70.55 (70.75)	6.75 (6.65)	1.65 (1.75)		1 778s (1 774s)		1 753s (1 752s)		1770 (1768)	588 (136)
$[Co(4\text{-}ClC_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$[g]	109	122.7	69.00 (69.25)	6.20 (6.45)	1.90 (1.70)		1 781s (1 775s)		1 754s (1 746s)		1765 (1757)	590 (158)
$[Co(4\text{-}FC_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	123	113.0	69.75 (70.00)	6.50 (6.50)	1.75 (1.75)	1 780sh (1 778sh)		1 763s (1 759s)			1763 (1759)	588 (150)
$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4][BPh_4]_2$	123	127.4	64.30 (64.05)	7.05 (7.30)	1.90 (1.90)		1 785s (1 775s)		1 765s (1 758s)		1778 (1764)	553 (189)
$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OMe)_3\}_4][BPh_4]_2$	125	123.7	61.45 (61.30)	6.30 (6.35)	2.05 (2.15)		1 798s (1 793s)		1 770m (1 769m)		1787 (1784)	546 (177)

[a] In nitromethane solution (10^{-3} mol dm^{-3}), at 25 °C. [b] Calculated values in parentheses. [c] In CH_2Cl_2 (KBr). [d] See ref. 8 for calculations. [e] In $(CH_3)_2CO$. [f] The $[Co(4\text{-}CH_3C_6H_4N{\equiv}^{15}N)\{P(OEt)_2Ph\}_4][BPh_4]_2$ complex shows the ν(NN) bands (CH_2Cl_2) at 1 748s and 1 729s cm^{-1}, ν'(NN) = 1 739s cm^{-1}. [g] Cl, 2.40 (2.15)%.

Table 2. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. data

Compounds	$\delta(^1H)$[a,b] aromatic	OCH_2CH_3	CH_3	OCH_2CH_3	$^{31}P\text{-}\{^1H\}$ 34 °C δ[b]	spin system	−80 °C δ[b]	J/Hz
$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.42 (br), 6.85 (m)	3.99 (m)	2.49 (s)	1.23 (t)	+148 (br)	A_2B_2	δ_A = 160.6, δ_B = 138.0	J_{AB} = 80.3
$[Co(3\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.44 (br), 6.86 (m)	4.06 (m)	2.36 (s)	1.19 (t)	+148 (br)	A_2B_2	δ_A = 160.6, δ_B = 137.7	J_{AB} = 82.0
$[Co(2\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.45 (br), 6.85 (m)	4.03 (m)	2.47 (s)	1.24 (t)	+147 (br)	A_2B_2	δ_A = 160.0, δ_B = 136.9	J_{AB} = 81.7
$[Co(4\text{-}CH_3OC_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.40 (br), 6.86 (m)	3.97 (m)	3.89 (s)	1.22 (t)	+148 (br)	A_2B_2	δ_A = 161.0, δ_B = 137.5	J_{AB} = 82.1
$[Co(C_6H_5N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.43 (br), 6.86 (m)	4.02 (m)		1.25 (t)	+148 (br)	A_2B_2	δ_A = 160.2, δ_B = 137.8	J_{AB} = 83.2
$[Co(4\text{-}ClC_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.55 (br), 7.31 (br), 6.82 (m)	4.06 (m)		1.27 (t)	+147 (br)	A_2B_2	δ_A = 160.1, δ_B = 139.1	J_{AB} = 80.5
$[Co(4\text{-}FC_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$	7.44 (br), 6.87 (m)	4.06 (m)		1.27 (t)	+148 (br)	A_2B_2	δ_A = 160.2, δ_B = 138.2	J_{AB} = 83.5
$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4][BPh_4]_2$	7.43 (br), 6.85 (m)	4.03 (m)	2.49 (s)	1.25 (t)	+129 (br), +110 (br)	A_2B_2	δ_A = 127.4, δ_B = 111.9	J_{AB} = 116
$[Co(4\text{-}CH_3C_6H_4N_2)\{P(OMe)_3\}_4][BPh_4]_2$[c]	7.31 (br), 6.89 (m)		2.44 (s)	3.57 (m)		A_2B_2	δ_A = 133.2, δ_B = 113.9	J_{AB} = 108

[a] At room temperature. [b] In $(CD_3)_2CO$. [c] In CD_2Cl_2.

Berry pseudo-rotation process,[18] which probably applies to the present exchange.

Table 1 shows that ν′(NN) in the $[Co(RN_2)\{P(OEt)_2Ph\}_4]^{2+}$ cations does not seem to be very sensitive to the nature of the substituent on the phenyl rings of the arenediazonium ligand. However, the slight changes are in the expected order, and the ν′(NN) value (1 778 cm^{-1}) for $[Co(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]^{2+}$ is also slightly higher than in the corresponding $P(OEt)_2Ph$ derivative, in agreement with the better π-acceptor properties of the $P(OEt)_3$ phosphite ligand. Finally, the high ν(NN) value for the present complexes as compared to the aryldiazenido derivatives of 3*d* transition metals such as $[Fe(CO)_2(PhN_2)(PPh_3)_2]^+$ [ν(NN) 1 724 cm^{-1}],[2c,14] $[FeX(4\text{-}CH_3C_6H_4N_2)(CO)(PPh_3)_2]$ (X = Cl or Br) [ν(NN) 1 640 cm^{-1}],[19] and $[Mn(CO)_2(PhN_2)(PPh_3)_2]$[ν(NN) 1 612, 1 543, 1 476 cm^{-1}][20] may partly be accounted for by the positive charge on the complexes, resulting in decreased back-bonding from the metal to the RN_2^+ group.

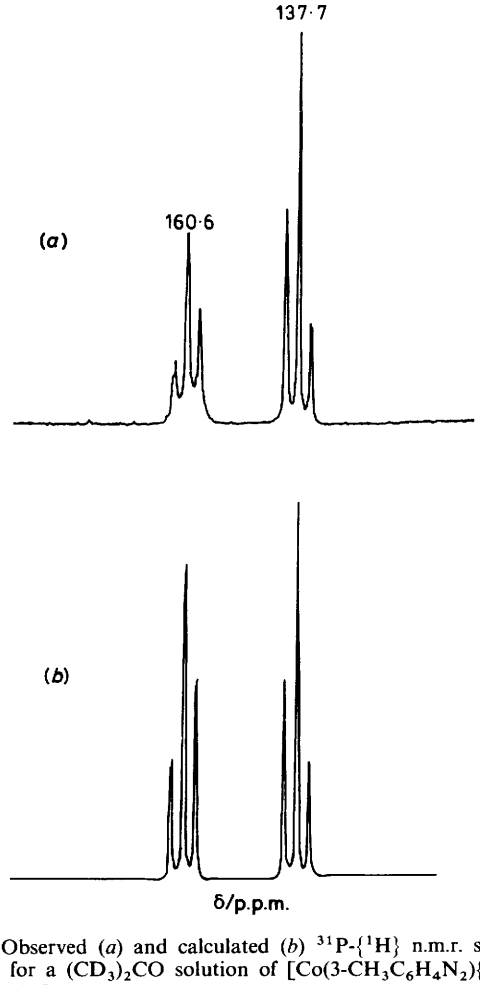


Figure. Observed (*a*) and calculated (*b*) $^{31}P\text{-}\{^1H\}$ n.m.r. spectra at −80 °C for a $(CD_3)_2CO$ solution of $[Co(3\text{-}CH_3C_6H_4N_2)\{P(OEt)_2Ph\}_4][BPh_4]_2$

The $[Co(RN_2)L_4]^{2+}$ complexes react at room temperature with CO (1 atm) rapidly and almost quantitatively to give monocarbonyl cations $[Co(CO)L_4]^+$ which further react with carbon monoxide to produce the final product, $[Co(CO)_2L_3]^+$ Nitric oxide also reacts under mild conditions (25 °C, 1 atm) with the arenediazonium complexes, but yields dinitrosyl compounds $[CoL_2(NO)_2]^+$.

The reaction of these arenediazonium derivatives in CH_2Cl_2 solution with 4-tolyl isocyanide can be conveniently followed by i.r. spectra. Addition of RNC (in either stoicheiometric or excess amounts) to $[Co(RN_2)L_4]^{2+}$ [L = $P(OEt)_2Ph$] solution shows the disappearance of the ν(NN) bands at 1 754—1 782 cm^{-1}, while three new absorptions in the ν(CN) stretching region at 2 073, 2 035, and 2 113 cm^{-1} appear in the i.r. spectra. The bands at 2 073 and 2 035 cm^{-1} are due to the previously reported[21] complex $[Co(RNC)_2L_3]^+$, while that at 2 113 cm^{-1} may be attributed to the monoisonitrile derivative $[Co(RNC)L_4]^+$. It should also be noted that, operating with a low isocyanide:complex ratio (0.5:1), the two complexes $[Co(RNC)L_4]^+$ and $[Co(RNC)_2L_3]^+$ are always present in the solution and attempts to separate them by chromatography or fractioned crystallization only gives the di-isocyanide compound in pure form, as $[Co(RNC)L_4]^+$ decomposes during separation.

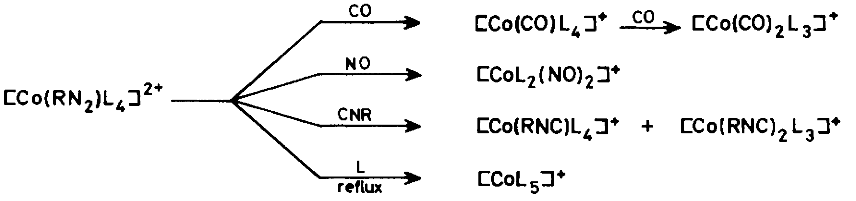
The reactivity of the cation $[Co(RN_2)L_4]^{2+}$ towards phosphite was also studied by varying the complex:phosphite ratio in the range 1:1 to 1:10, but at room temperature no reaction was observed. By warming the solution, however, substitution of the RN_2^+ ligand with phosphite takes place to give the $[CoL_5]^+$ cation, which can be isolated and characterized. All these reactions, summarized in the Scheme, show that the arenediazonium ligand is a relatively good leaving group in these cobalt complexes and can easily be substituted by several π-acceptor ligands.

These results appear to contradict the properties shown by arenediazonium complexes of other metals[2,19] such as Fe, Ru, Rh, Os, *etc.* in which reactivity studies indicate that the RN_2^+ ligand is inert to substitution.

The reaction of the cation $[Co(RN_2)L_4]^{2+}$ in acetone–ethanol with lithium chloride (both in stoicheiometric and in excess amounts) proceeds slowly to afford the five-co-ordinate Co^{II} complexes[22] $[CoClL_4]^+$, which can be isolated (yield 80%) and characterized. G.l.c. analysis of the solution at the end of the reaction shows that hydrocarbon RH is also formed as a product. These data can be interpreted in terms of reaction (4) in

$$[Co(RN_2)L_4]^{2+} + Cl^- \xrightarrow{\text{solvent}} [CoClL_4]^+ + N_2 + RH \qquad (4)$$

which the co-ordinated arenediazonium ligand oxidizes the central metal to Co^{II}, giving N_2 and the unstable radical R$^\bullet$. Presumably by abstraction of a hydrogen atom from the solvent, the intermediate R$^\bullet$ gives the observed hydrocarbon. Electron transfer between the metal and the RN_2^+ moiety in M-NNR systems is a feature which has been previously observed[23] in arenediazonium complexes of ruthenium, and reduction at co-ordinated arenediazonium leads to unstable intermediates which



Scheme.

have low-energy pathways for decomposition *via* N_2 and aryl radicals.

It was hoped that these arenediazonium derivatives of cobalt(I) would undergo protonation reactions with hydrogen chloride or HBF_4 to give aryldi-imine complexes. Although colour change was observed when a dichloromethane solution of $[Co(RN_2)L_4]^{2+}$ was treated with dry gaseous HCl or with HBF_4, no stable products could be isolated.

A comparison of arenediazonium complexes $[Co(RN_2)L_4]^{2+}$ with the related nitrosyl complexes $[CoL_4(NO)]^{2+}$, previously reported by us,[5b] shows that both exhibit, in solution, fluxional behaviour and, at -80 °C, trigonal-bipyramidal geometry with the NO or $RN_2{}^+$ ligand in equatorial position for both types of complexes. The ν(NO) values for the nitrosyls (range 1 819—1 835 cm^{-1}) are *ca.* 60 cm^{-1} higher than ν(NN) (Table 1), as generally observed for electronically and structurally equivalent nitrosyl and arenediazonium complexes and, although the crystal structure is not known, spectroscopic data strongly suggest a formal NO^+ and RNN^+ ligand in the case of a d^8 Co^I central metal. However, reactivity studies indicate that, while substitution of the $RN_2{}^+$ ligand is easy, the nitrosyl group can be replaced only by the isocyanide ligand. Furthermore, different behaviour is shown in reactions towards halide ions, which allowed the $[CoClL_3(NO)]^+$ compounds[5c] to be prepared in the case of the nitrosyls, whereas oxidation of the metal by the arenediazonium ligand affording $[CoClL_4]^+$ cation takes place in the $[Co(RN_2)L_4]^{2+}$ complexes.

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