

## Polynuclear Carbonyl Complexes of Cobalt containing Isocyanides and Other Ligands

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Isocyanides, RNC (R = alkyl but usually Me or Bu<sup>t</sup>), displace up to five carbonyl ligands from [Co<sub>4</sub>(CO)<sub>12</sub>], [(π-C<sub>5</sub>H<sub>5</sub>)NiCo<sub>3</sub>(CO)<sub>9</sub>], [YCCo<sub>3</sub>(CO)<sub>9</sub>] (Y = Cl, Me, or Ph), [SCo<sub>3</sub>(CO)<sub>9</sub>], and [SCo<sub>3</sub>Fe(CO)<sub>9</sub>]. The reactions usually take place under mild conditions with retention of the pseudotetrahedral XCo<sub>3</sub> or SCo<sub>2</sub>Fe cluster (X = Co, Ni, C, or S). With octacarbonyldicobalt, the products are derivatives of [Co<sub>4</sub>(CO)<sub>12</sub>] or [(RNC)<sub>5</sub>Co][Co(CO)<sub>4</sub>], but never of [Co<sub>2</sub>(CO)<sub>8</sub>]. [{LCo(CO)<sub>3</sub>}]<sub>2</sub>Hg (L = tertiary phosphine or CO) and [(R<sub>3</sub>P)<sub>2</sub>Co(CO)<sub>3</sub>][Co(CO)<sub>4</sub>] salts undergo similar CO replacement reactions. The structures of the products are discussed on the bases of their i.r. spectra.

THE replacement of carbon monoxide in various polynuclear cobalt carbonyls by Group VA ligands may take place with (a) retention of the cluster,<sup>1</sup> or (b) its fragmentation into simpler units.<sup>2</sup> The related reactions using organoisocyanide ligands have received far less attention. The investigations described in the present paper show that they are much less likely to take place by route (b), and in some instances occur with polymerisation of dicobalt to tetracobalt species. Previous work has shown that under vigorous conditions octacarbonyldicobalt and methyl isocyanide give [(MeNC)<sub>5</sub>Co][Co(CO)<sub>4</sub>].<sup>3</sup>

<sup>1</sup> G. Cetini, O. Gambino, R. Rossetti, and P. L. Stanghellini, *Inorg. Chem.*, 1968, **7**, 609.

<sup>2</sup> W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

<sup>3</sup> A. Sacco, *Gazzetta*, 1953, **83**, 632; W. Hieber and J. Sedlmeier, *Chem. Ber.*, 1954, **87**, 787.

<sup>4</sup> *Org. Synth.*, **41**, 13; and **46**, 75.

<sup>5</sup> R. B. King, *Organometallic Synth.*, 1965, **1**, 103.

<sup>6</sup> A. T. T. Hsieh and J. Knight, *J. Organometallic Chem.*, 1971, **26**, 125.

<sup>7</sup> L. Markó, G. Bor, and E. Klumpp, *Chem. and Ind.*, 1961, 1491.

### EXPERIMENTAL

Published methods were used to prepare the organoisocyanides,<sup>4</sup> [Co<sub>4</sub>(CO)<sub>12</sub>],<sup>5</sup> [(π-C<sub>5</sub>H<sub>5</sub>)NiCo<sub>3</sub>(CO)<sub>9</sub>],<sup>6</sup> [SCo<sub>3</sub>(CO)<sub>9</sub>],<sup>7</sup> [SFeCo<sub>2</sub>(CO)<sub>9</sub>],<sup>8</sup> [MeCCo<sub>3</sub>(CO)<sub>9</sub>],<sup>9</sup> [PhCCo<sub>3</sub>(CO)<sub>9</sub>],<sup>9</sup> [ClCCo<sub>3</sub>(CO)<sub>9</sub>],<sup>9</sup> [{Ph<sub>3</sub>PCo(CO)<sub>3</sub>}]<sub>2</sub>,<sup>10</sup> [{(Bu<sup>n</sup>)<sub>3</sub>PCo(CO)<sub>3</sub>}]<sub>2</sub>,<sup>11</sup> [{Co(CO)<sub>4</sub>}]<sub>2</sub>Hg,<sup>12</sup> [{Ph<sub>3</sub>PCo(CO)<sub>3</sub>}]<sub>2</sub>Hg,<sup>13</sup> and [{Bu<sub>3</sub>PCo(CO)<sub>3</sub>}]<sub>2</sub>Hg.<sup>13</sup> Other chemicals were purchased.

All reactions were carried out in purified solvents under an atmosphere of nitrogen at room temperature using ca. 1–2 g of the metal carbonyl complex unless it is stated otherwise. They were monitored by i.r. spectroscopy. When the reactions were complete, the products were separated by chromatography on alumina using benzene-hexane mixtures as eluants, or by crystallization. They were purified by recrystallization.

<sup>8</sup> S. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometallic Chem.*, 1964, **1**, 372.

<sup>9</sup> R. B. King, *Organometallic Synth.*, 1965, **1**, 153.

<sup>10</sup> W. Hieber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230.

<sup>11</sup> F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc. (A)*, 1966, 1052.

<sup>12</sup> S. V. Dighe and M. Orchin, *Inorg. Chem.*, 1962, **1**, 965.

<sup>13</sup> F. Bonati, S. Cenini, and R. Ugo, *J. Chem. Soc. (A)*, 1967, 932.

Melting points, analyses, and infrared spectra (1700–2200 cm<sup>-1</sup>) of compounds described in the text

| Analyses <sup>a</sup>   |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
|---|---|-------------------|-------------------|------|-----|---------------------|------|-----|----------------|---|----------------|---------------------|------------|-------------|--|
| Compound <sup>a</sup>   |   |                   | Found (%)         |      |     | Others and <i>M</i> |      |     | Calculated (%) |   |                | Others and <i>M</i> |            |             |  |
| R   | n | Y                 | C                 | H    | N   | C                   | H    | N   | C              | H | N              | C                   | H          | N           |  |
| [Co <sub>2</sub> (CO) <sub>12-n</sub> (CNR) <sub><i>n</i></sub> ]   |   |                   | M.p. <sup>b</sup> |      |     |                     |      |     |                |   |                |                     |            |             |  |
| Me  | 1 |                   | 142–144           | 26.3 | 0.6 | 2.8                 | 26.7 | 0.5 | 2.5            |   |                | 1845sh              | 1850 (9.3) | 1860 (10)   |  |
| Et  | 1 |                   | dec. 200          | 27.1 | 0.9 | 2.2                 | 28.0 | 0.8 | 2.3            |   |                | 1844sh              | 1848 (9.6) | 1857 (10)   |  |
| But   | 1 |                   | 106–108           | 30.6 | 1.4 | 2.4                 | 30.6 | 1.4 | 2.2            |   |                | 1845sh              | 1850 (9.0) | 1867 (10)   |  |
| Cy  | 1 |                   | 115–117           | 32.6 | 2.0 | 2.1                 | 33.1 | 1.7 | 2.1            |   | <i>M</i> = 627 | 1845sh              | 1849 (9.4) | 1857 (10)   |  |
| PhCH <sub>2</sub>   | 1 |                   | dec. 270          | 33.8 | 1.6 | 2.3                 | 34.5 | 1.1 | 2.1            |   |                | 1845sh              | 1850 (7.0) | 1858 (10)   |  |
| Me  | 2 |                   | 128–130           | 27.8 | 1.0 | 4.8                 | 28.1 | 1.0 | 4.7            |   |                | 1832 (10)           | 1844 (8.4) | 1875 (0.5)  |  |
| Et  | 2 |                   | 50–51             | 30.4 | 1.6 | 4.5                 | 30.6 | 1.6 | 4.5            |   |                | 1835 (10)           | 1844 (9.2) | 1876 (0.5)  |  |
| But   | 2 |                   | 87–89             | 35.2 | 2.7 | 4.1                 | 35.2 | 2.6 | 4.1            |   | <i>M</i> = 682 | 1836 (10)           | 1844 (9.3) | 1876 (0.4)  |  |
| Cy  | 2 |                   | 66–68             | 39.6 | 3.3 | 4.0                 | 39.3 | 3.0 | 3.8            |   |                | 1835 (10)           | 1842 (9.3) | 1876 (0.7)  |  |
| PhCH <sub>2</sub>   | 2 |                   | 40–42             | 41.4 | 2.2 | 3.6                 | 41.6 | 1.8 | 3.5            |   |                | 1836 (9.4)          | 1845 (10)  | 1876 (0.4)  |  |
| Me  | 3 |                   | 80–81             | 29.4 | 1.6 | 7.2                 | 29.4 | 1.5 | 6.9            |   |                | 1825 (9.2)          | 1833 (10)  | 1865 (0.5)  |  |
| Et  | 3 |                   | 137–139           | 38.9 | 3.7 | 5.6                 | 39.1 | 3.7 | 5.7            |   | <i>M</i> = 737 | 1823 (9.5)          | 1831 (10)  | 1864 (0.5)  |  |
| But   | 3 |                   | 82–83             | 43.7 | 4.5 | 5.3                 | 44.2 | 4.1 | 5.2            |   |                | 1822 (9.3)          | 1830 (10)  | 1864 (0.5)  |  |
| Cy  | 3 |                   | dec. 200          | 30.3 | 1.9 | 9.1                 | 30.8 | 1.9 | 9.0            |   | <i>M</i> = 792 | 1794sh              | 1803 (10)  | 1843 (0.05) |  |
| Me  | 4 |                   | dec. 156          | 42.3 | 4.6 | 7.0                 | 42.4 | 4.6 | 7.1            |   |                | 1813 (9.8)          | 1820 (10)  | 1845 (4.3)  |  |
| Et  | 4 |                   | 96–98             | 48.1 | 4.9 | 6.0                 | 48.2 | 4.9 | 6.2            |   | <i>M</i> = 847 | 1810 (10)           | 1817 (9.8) | 1845 (4.0)  |  |
| Cy  | 4 |                   | 177–178           | 44.9 | 5.3 | 8.1                 | 45.3 | 5.3 | 8.2            |   |                | 1784sh              | 1793sh     | 1802 (10)   |  |
| But   | 5 |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| [( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )NiCo <sub>2</sub> (CO) <sub>8-n</sub> (CNR) <sub><i>n</i></sub> ] |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| Me  | 1 |                   | 114–115           | 35.1 | 2.3 | 2.1                 | 35.5 | 2.3 | 2.3            |   |                | 1830sh              | 1838 (4.7) | 1845 (4.3)  |  |
| But   | 1 |                   |                   |      |     |                     |      |     |                |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| [YCo <sub>2</sub> (CO) <sub>8-n</sub> (CNR) <sub><i>n</i></sub> ]   |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| Me  | 1 | Me                | 55–56             | 31.2 | 1.3 | 3.0                 | 30.8 | 1.3 | 3.0            |   |                | 1830sh              | 1838 (4.7) | 1845 (4.3)  |  |
| But   | 1 | Ph                | 80–82             | 42.1 | 2.4 | 2.5                 | 41.9 | 2.4 | 2.4            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| Me  | 1 | Cl                | 68–69             | 26.5 | 0.4 | 2.9                 | 27.0 | 0.6 | 2.9            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| Me  | 2 | Me                | 37–38             | 31.9 | 1.8 | 5.7                 | 32.4 | 2.1 | 5.8            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 2 | Ph                | 78–79             | 45.6 | 3.5 | 4.2                 | 45.9 | 3.7 | 4.4            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| Me  | 2 | Cl                | 44–46             | 29.2 | 1.3 | 5.4                 | 28.7 | 1.2 | 5.6            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 2 | Cl                | 23–24             | 36.5 | 3.6 | 4.6                 | 36.8 | 3.1 | 4.8            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| Me  | 3 | Me                | 88–89             | 33.4 | 2.4 | 8.4                 | 33.9 | 2.4 | 8.5            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 3 | Me                | 133–134           | 44.6 | 4.6 | 6.7                 | 44.4 | 4.8 | 6.8            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 3 | Ph                | 72–74             | 49.9 | 4.2 | 5.8                 | 49.2 | 4.7 | 6.1            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| Me  | 3 | Cl                | 200               | 34.4 | 3.8 | 6.5                 | 34.4 | 2.7 | 7.5            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 3 | Cl                | 103–104           | 41.5 | 4.5 | 6.5                 | 41.2 | 4.4 | 6.5            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 4 | Ph                | 94–96             | 52.9 | 5.2 | 7.4                 | 52.0 | 5.5 | 7.6            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 4 | Cl                | 88–89             | 44.3 | 4.7 | 7.6                 | 44.8 | 5.2 | 8.0            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| [SFeCo <sub>2</sub> (CO) <sub>8-n</sub> (CNR) <sub><i>n</i></sub> ]   |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| But   | 2 |                   | 85–86             | 35.4 | 4.0 | 4.7                 | 35.9 | 3.2 | 4.9            |   | <i>S</i> = 5.6 | 1830sh              | 1838 (5.0) | 1845 (4.3)  |  |
| But   | 3 |                   | 90–91             | 40.4 | 4.4 | 6.5                 | 40.4 | 4.3 | 6.7            |   | <i>S</i> = 5.1 | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| [(Ph <sub>3</sub> P) <sub>2</sub> Co(CNR) <sub>2</sub> ][Co(CO) <sub>4</sub> ]                                |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| Me  | 2 |                   | 174–176           | 63.0 | 4.8 | 4.4                 | 62.9 | 4.5 | 4.8            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.3)  |  |
| Et  | 2 |                   | 162–164           | 63.6 | 5.3 | 4.5                 | 64.0 | 4.9 | 4.6            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| Cy  | 2 |                   | 138–139           | 67.2 | 5.6 | 3.8                 | 67.7 | 5.8 | 3.9            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| [(Bun <sub>3</sub> P) <sub>2</sub> Co(CNR) <sub>2</sub> ][BPh <sub>4</sub> ]                                  |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| Me  | 2 |                   | 122–124           | 72.8 | 9.8 | 4.4                 | 71.6 | 9.2 | 4.6            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| [Y <sub>2</sub> Co <sub>2</sub> (CO) <sub>8-n</sub> (CNR) <sub><i>n</i></sub> Hg]                             |   |                   |                   |      |     |                     |      |     |                |   |                |                     |            |             |  |
| Me  | 2 | CO                | 137–128           | 20.6 | 0.8 | 4.8                 | 21.2 | 1.1 | 4.9            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.3)  |  |
| Me  | 1 | Bu <sub>3</sub> P | 41.8              | 6.6  | 1.6 | 41.2                | 6.3  | 1.6 | 4.8            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |
| But   | 2 | Ph <sub>3</sub> P | 216–219           | 53.7 | 4.4 | 2.4                 | 53.6 | 4.3 | 2.5            |   |                | 1830sh              | 1838 (5.0) | 1845 (4.0)  |  |

| Compound <sup>a</sup>   |                |                                | Absorption bands <sup>d</sup> |             |
|---|----------------|--------------------------------|-------------------------------|-------------|
| R   | n              | Y                              |                               |             |
| [Co <sub>2</sub> (CO) <sub>8</sub> ] <sub>2</sub> -n(CNR) <sub>m</sub>                        |                |                                |                               |             |
| Me  | 1              |                                | 2040 (31-0)                   | 2046 (37-0) |
| Et  | 1              |                                | 2039 (30-0)                   | 2045 (34-5) |
| But   | 1              |                                | 2040 (29-0)                   | 2046 (34-0) |
| Cy  | 1              |                                | 2039 (35-6)                   | 2045 (39-4) |
| PhCH <sub>2</sub>   | 1              |                                | 2041 (31-0)                   | 2045 (37-0) |
| Me  | 2              |                                | 2070 (5-6)                    |             |
| Et  | 2              |                                | 2069 (6-6)                    |             |
| But   | 2              |                                | 2067 (6-8)                    |             |
| Cy  | 2              |                                | 2067 (7-0)                    |             |
| PhCH <sub>2</sub>   | 2              |                                | 2069 (8-3)                    |             |
| Me  | 3              |                                |                               |             |
| But   | 3              |                                |                               |             |
| Cy  | 3              |                                |                               |             |
| Me  | 4              |                                | 2025 (16-0)                   |             |
| But   | 4              |                                | 2021 (6-4)                    |             |
| Cy  | 4              |                                | 2018 (5-8)                    |             |
| But   | 5 <sup>e</sup> |                                | 1997 (12-4)                   | 2020 (3-3)  |
| [(π-C <sub>5</sub> H <sub>5</sub> )NiCo <sub>2</sub> (CO) <sub>8</sub> -n(CNR) <sub>m</sub> ] |                |                                |                               |             |
| Me  | 1              |                                | 2065 (1-0)                    |             |
| But   | 1              |                                | 2064 (0-8)                    |             |
| [YCo <sub>2</sub> (CO) <sub>8</sub> -n(CNR) <sub>m</sub> ]                                    |                |                                |                               |             |
| Me  | 1              |                                | 2030 (8-0)                    | 2037 (10)   |
| But   | 1              |                                | 2030 (9-1)                    | 2038 (10)   |
| Me  | 1              | Ph                             | 2047 (1-0)                    | 2089 (2-9)  |
| Me  | 2              | Me                             | 2010 (5-3)                    | 2056 (2-6)  |
| Me  | 2              | Ph                             | 2020sh                        | 2053 (3-8)  |
| Me  | 2              | Cl                             | 2062sh                        | 2066 (3-5)  |
| Me  | 2              | Cl                             | 2057sh                        | 2061 (2-9)  |
| Me  | 3              | Me                             | 2003sh                        | 2021 (3-6)  |
| But   | 3              | Me                             | 2000sh                        | 2017 (2-6)  |
| But   | 3              | Ph                             | 1998sh                        | 2019 (4-1)  |
| Me  | 3              | Cl <sup>f</sup>                | 2012sh                        | 2034 (3-7)  |
| But   | 3              | Cl                             | 2011sh                        | 2011sh      |
| But   | 4              | Ph                             | 1994 (7-8)                    |             |
| But   | 4              | Cl                             | 2007 (7-3)                    |             |
| [(SF <sub>5</sub> Co <sub>2</sub> (CO) <sub>8</sub> -n(CNR) <sub>m</sub> ]                    |                |                                |                               |             |
| But   | 2              |                                | 2027sh                        | 2054 (3-1)  |
| But   | 3              |                                | 2016 (5-8)                    | 2029 (5-0)  |
| [(Ph <sub>3</sub> P) <sub>2</sub> Co(CNR) <sub>3</sub> ][Co(CO) <sub>4</sub> ]                |                |                                |                               |             |
| Me <sup>g</sup>   |                |                                |                               |             |
| Et <sup>g</sup>   |                |                                |                               |             |
| Cy <sup>g</sup>   |                |                                |                               |             |
| [(Bu <sub>2</sub> P) <sub>2</sub> Co(CNR) <sub>3</sub> ][BPh <sub>4</sub> ]                   |                |                                |                               |             |
| Me <sup>e</sup>   |                |                                |                               |             |
| [Y <sub>2</sub> Co <sub>2</sub> (CO) <sub>8</sub> -n(CNR) <sub>m</sub> Hg]                    |                |                                |                               |             |
| Me  | 2              | CO <sup>e</sup>                | 2035 (1-3)                    |             |
| Me  | 1              | Bu <sub>2</sub> P <sup>e</sup> | 1944 (8-9)                    |             |
| But   | 2              | Ph <sub>3</sub> P <sup>e</sup> | 2059 (1-1)                    |             |

<sup>a</sup> Cy = cyclohexyl. <sup>b</sup> Determined in sealed tubes. <sup>c</sup> dec. = decomposed without melting. <sup>d</sup> M = molecular weight determined cryoscopically in benzene. <sup>e</sup> Peak positions (cm<sup>-1</sup>) with relative peak heights in parentheses. Hexane solution unless stated otherwise. <sup>f</sup> sh = shoulder, s = strong, m = medium, and w = weaker. <sup>g</sup> i.r. spectrum in chloroform solution. <sup>h</sup> Crystallizes as [Co<sub>2</sub>(CO)<sub>8</sub>(CNMe)<sub>3</sub>]<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. <sup>i</sup> i.r. spectrum of Nujol mull.

The reactions between  $[\text{Co}_4(\text{CO})_{12}]$  and the isocyanide RNC were carried out in benzene with the slow, dropwise addition of a solution of the ligand to a well-stirred solution of the complex. They were virtually instantaneous and proceeded by stepwise substitution. Thus the use of RNC :  $[\text{Co}_4(\text{CO})_{12}]$  mole ratios of  $n : 1$  gave nearly pure  $\text{Co}_4(\text{CO})_{12-n}(\text{CNR})_n$  in yields of 60–70% for  $n = 1$ –4. The procedure prevented the formation of the  $[(\text{RNC})_5\text{Co}][\text{Co}(\text{CO})_4]$  salts which otherwise took place at higher concentrations.  $[\text{Co}_4(\text{CO})_7(\text{CNBu}^t)_5]$  was obtained from  $[\text{Co}_4(\text{CO})_8(\text{CNBu}^t)_4]$  and  $\text{Bu}^t\text{NC}$  (mole ratio 1 : 6).

Octacarbonyldicobalt and RNC (mole ratio 2 :  $n$ ) gave  $[\text{Co}_4(\text{CO})_{12-n}(\text{CNR})_n]$  ( $n = 2$ –4). There was no evidence for the formation of any other products except  $[(\text{RNC})_5\text{Co}][\text{Co}(\text{CO})_4]$ . Even very low concentrations of isocyanide gave no more than traces of  $[\text{Co}_4(\text{CO})_{11}(\text{CNR})]$ .

In contrast, when solutions or suspensions of  $[\{\text{LCo}(\text{CO})_3\}_2]$  in benzene ( $\text{L} = \text{Ph}_3\text{P}$  or  $\text{Bu}^t_3\text{P}$ ) were refluxed with isocyanides for 1 h (mol ratio 1 : 3), yellow salts  $[\text{L}_2\text{Co}(\text{CNR})_3][\text{Co}(\text{CO})_4]$  were obtained ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{C}_6\text{H}_{11}$ ). They were isolated as such or as  $[\text{L}_2\text{Co}(\text{CNR})_3][\text{BPh}_4]$  by crystallization from acetone (yields 70–80%). When  $\text{L} = \text{Bu}^t_3\text{P}$ , there was evidence for the formation of cations containing carbonyl ligands.

$[(\pi\text{-C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_9]$  (0.3 g) and  $\text{Bu}^t\text{NC}$  (0.6 ml) in benzene (25 ml) were stirred for 2 h to give  $[(\pi\text{-C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_8(\text{CNBu}^t)]$  (50% yield) and  $[\text{Co}_4(\text{CO})_{12-n}(\text{CN}^t\text{Bu})_n]$  ( $n = 2$  or 3). The direct reaction of  $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CNC}_6\text{H}_{11})_2]$  and  $\text{Co}_2(\text{CO})_8$  gave  $[\text{Co}_4(\text{CO})_{12-n}(\text{CNC}_6\text{H}_{11})_n]$  and  $[\text{Ni}(\pi\text{-C}_5\text{H}_5)_2]$ .

Although  $[\text{SCo}_3(\text{CO})_9]$  reacted with  $\text{Bu}^t\text{NC}$ , no product could be isolated. However with the more stable  $[\text{SFeCo}_2(\text{CO})_9]$ ,  $[(\text{Bu}^t\text{NC})\text{Fe}(\text{CO})_4]$  and  $[\text{SFeCo}_2(\text{CO})_{9-n}(\text{CNBu}^t)_n]$  ( $n = 2$  or 3) were obtained.

When hexane solutions of  $[\text{MeCCo}_3(\text{CO})_9]$  (0.5 g) and RNC ( $\text{R} = \text{Me}$  or  $\text{Bu}^t$ ), mol ratio 1 : 6, were refluxed for 1–1½ h, mixtures  $[\text{MeCCo}_3(\text{CO})_{9-n}(\text{CNR})_n]$  ( $n = 1$ –3) were obtained. Yields of the purified products were 15–50%.

$[\text{PhCCo}_3(\text{CO})_{9-n}(\text{CNBu}^t)_n]$ , ( $n = 1$ –4) could be prepared similarly or by stirring the reaction mixtures for 20 h.  $[\text{ClCCo}_3(\text{CO})_9]$  reacted rapidly with isocyanides in hexane. By using suitable proportions of reactants, pure  $[\text{ClCCo}_3(\text{CO})_{9-n}(\text{CNR})_n]$  could be isolated without the aid of chromatography in yields of 30–40% ( $n = 1$ –4;  $\text{R} = \text{Me}$  or  $\text{Bu}^t$ ).

Methyl isocyanide and  $[\{\text{Co}(\text{CO})_4\}_2\text{Hg}]$  (mol ratio 2 : 1) reacted rapidly in benzene to give  $[\{\text{MeNC}\text{Co}(\text{CO})_3\}_2\text{Hg}]$  (yield ca. 40%). Under the same conditions,  $[\{\text{Bu}^t_3\text{PCo}(\text{CO})_3\}_2\text{Hg}]$  and  $\text{MeNC}$ , or  $[\{\text{Ph}_3\text{PCo}(\text{CO})_3\}_2\text{Hg}]$  and  $\text{Bu}^t\text{NC}$  gave  $[\{\text{Bu}^t_3\text{PCo}(\text{CO})_3\}_2\text{Hg}][\text{Co}(\text{CO})_2(\text{CNMe})\text{PBu}^t_3]$  or  $[\{\text{Ph}_3\text{P}(\text{Bu}^t\text{NC})\text{Co}(\text{CO})_2\}_2\text{Hg}]$  respectively in yields of ca. 70%. All three products were yellow solids which were recrystallized from benzene–hexane mixtures.

The complexes which have been isolated are listed in the Table together with their melting points, analyses, and i.r. spectra. The spectra were obtained as described previously.<sup>14</sup>

\* It is only when  $\text{R} = \text{Me}$  that the expected analyses for  $[\text{Co}_2(\text{CO})_{8-n}(\text{CNR})_n]$  and  $[\text{Co}_4(\text{CO})_{12-n}(\text{CNR})_n]$  ( $n = 2m$ ) differ to any great extent.

<sup>14</sup> J. Newman and A. R. Manning, *J.C.S. Dalton*, 1973, 1593.

<sup>15</sup> J. Newman and A. R. Manning, unpublished work.

<sup>16</sup> M. J. Boylan, J. Bellerby, J. Newman, and A. R. Manning, *J. Organometallic Chem.*, 1973, 47, C33.

## RESULTS AND DISCUSSION

Whereas the ionic products and the derivatives of mercury cobalt carbonyl are yellow, air-stable solids, the polynuclear compounds are deeply coloured solids or liquids;  $[\text{Co}_4(\text{CO})_{12-n}(\text{CNR})_n]$  ( $\text{R} = \text{alkyl}$ ;  $n = 1$ –5) are dark brown,  $[(\pi\text{-C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_8(\text{CNBu}^t)]$  is green,  $[\text{YCCo}_3(\text{O})_{9-n}(\text{CNR})_n]$  ( $\text{Y} = \text{Me}$ ,  $\text{Ph}$  or  $\text{Cl}$ ) purple, and  $[\text{SFeCo}_2(\text{CO})_{9-m}(\text{CMR})_m]$  ( $m = 2$  or 3) are brown. All are at least as stable as their unsubstituted precursors towards thermal and oxidative decomposition. Although this increase in stability is especially marked for the derivatives of dodecacarbonyltetracobalt, the ability of isocyanide ligands to stabilize clusters of the first-row transition metals appears to be widespread.<sup>15</sup>

In a preliminary publication, the  $[\text{Co}_4(\text{CO})_{12-n}(\text{CNR})_n]$  complexes were formulated as derivatives of octacarbonyldicobalt,  $[\text{Co}_2(\text{CO})_{8-m}(\text{CNR})_m]$ .<sup>16</sup> Their true natures were confirmed by molecular-weight measurements (cryoscopic in benzene<sup>17</sup>), whilst their i.r. spectra are consistent with molecular structures based on that of  $[\text{Co}_4(\text{CO})_{12}]$ .<sup>18,19</sup> The isocyanide molecules do not act as bridging ligands in these complexes (or in any other described here), but there are three types of terminal co-ordination positions which they may occupy. Thus although isomerism is possible, the simplicity of the spectra in the terminal C–O stretching region and the sharpness of most absorption bands suggests that one isomer predominates over the others in all complexes except those of the type  $[\text{Co}_4(\text{CO})_{10}(\text{CNR})_2]$ . With these, the terminal  $\nu(\text{CO})$  absorption band of highest frequency has two components which may be due to isomers (cf.  $[\text{Co}_4(\text{CO})_{10}(\text{PET}_3)_2]$  and  $[\text{Co}_4(\text{CO})_9(\text{PMe}_2\text{Ph})_3]$ <sup>20</sup>). The intense absorption bands in the  $\nu(\text{CO}_\mu)$  region of all spectra are probably due to the  $e$  vibrations of the  $\text{Co}_3(\mu\text{-CO})_3$  moiety which have been split into two components by the lowering of the molecular symmetries which take place on CO substitutions. The weak absorption band at higher frequency in many spectra is attributed to the  $\nu(\text{CO}_\mu)$  mode of  $a_1$  symmetry.

The structure of  $[(\pi\text{-C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_9]$  is similar to that of  $[\text{Co}_4(\text{CO})_{12}]$  but with the apical  $\text{Co}(\text{CO})_3$  moiety being replaced by  $(\pi\text{-C}_5\text{H}_5)\text{Ni}$ .<sup>6</sup> In the spectra of  $[(\pi\text{-C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_8(\text{CNR})]$ , the two components of the  $e$   $\nu(\text{CO}_\mu)$  mode have a separation comparable to that observed for  $[\text{Co}_4(\text{CO})_{11}(\text{CNR})]$ . This implies that in both series of compounds the isocyanide ligands are co-ordinated to a cobalt atom of the triangular  $\text{Co}_3(\mu\text{-CO})_3$  array.  $[(\pi\text{-mesitylene})\text{Co}_4(\text{CO})_9]$ <sup>21</sup> undergoes a similar substitution reaction, but no product was isolated.

The pseudotetrahedral  $\text{XCo}_3$  framework found in

<sup>17</sup> F. G. Mann and B. C. Saunders, 'Practical Organic Chemistry,' Longmans Green and Co., London, 1938, p. 319.

<sup>18</sup> C. W. Wei, *Inorg. Chem.*, 1969, 8, 2384.

<sup>19</sup> G. Bor, *Spectrochim. Acta*, 1963, 19, 1209.

<sup>20</sup> D. Labrousse and R. Poilblanc, *Inorg. Chim. Acta*, 1972, 6, 387.

<sup>21</sup> I. U. Khand, G. R. Knox, P. Pauson, and W. E. Watts, *J.C.S. Perkin I*, 1973, 975.



$[\text{Co}_4(\text{CO})_{12}]$  and  $[(\pi\text{-C}_5\text{H}_5)\text{NiCo}_3(\text{CO})_9]$  is retained in the  $[\text{YCCo}_3(\text{CO})_9]$  complexes, but these last do not possess bridging carbonyl groups.<sup>22</sup> As they have two types of terminal ligands, isomers are possible on CO substitution. They are probably responsible for the relative complexity of the i.r. spectra of those  $[\text{YCCo}_3(\text{CO})_{9-n}(\text{CNR})_n]$  derivatives where  $n = 1-4$  which often show more absorption bands due to their  $\nu(\text{CO})$  vibrations than they have CO ligands. In other instances two components are observed for the absorption bands at highest frequency which are almost certainly due to the singly degenerate, fully symmetric,  $\nu(\text{CO})$  vibrations of two different species which cannot be separated by chromatography. Isomerism is also exhibited by various  $[\text{YCCo}_3(\text{CO})_{9-n}\text{L}_n]$  complexes ( $\text{L} =$  tertiary phosphine or arsine), but for these C-O bridged isomers are often important.<sup>23</sup> Although no  $\mu\text{-CO}$  species have been observed in solutions of the isocyanide derivatives,  $[\text{MeCCo}_3(\text{CO})_6(\text{CNR})_3]$  ( $\text{R} = \text{Me}$  or  $\text{Bu}^t$ ) crystallize in a purple form having only terminal carbonyl groups and an orange form with terminal and bridging CO ligands.\*

$[\text{SFeCo}_2(\text{CO})_9]$  has a structure similar to those of the methynyl complexes.<sup>24</sup> The Mössbauer spectra of its derivatives  $[\text{SFeCo}_2(\text{CO})_{9-n}(\text{PPh}_3)_n]$  ( $n = 1$  or  $2$ ) show that substitution takes place on the cobalt atoms,<sup>25</sup> and the similarity of the i.r. spectra of  $[\text{SFeCo}_2(\text{CO})_7(\text{PPh}_3)_2]$  and  $[\text{SFeCo}_2(\text{CO})_7(\text{CNBu}^t)_2]$  suggests that the two have similar structures.  $[\text{SFeCo}_2(\text{CO})_6(\text{CNBu}^t)_3]$  exists as mixtures of isomers in solution; at least one has  $\mu\text{-CO}$  ligands.

Although  $[\text{SCo}_3(\text{CO})_9]$  undergoes CO substitution reactions with isocyanides, the products appear to be less stable than the precursor.

The initial products from the reactions of  $[\text{Co}_2(\text{CO})_8]$  with isocyanides are the  $[\text{Co}_4(\text{CO})_{12-n}(\text{CNR})_n]$  derivatives. If an excess of ligand and more vigorous conditions are used, the  $[\text{Co}(\text{CNR})_5][\text{Co}(\text{CO})_4]$  salts are obtained.<sup>3</sup> The only products obtained from  $[\{\text{LCo}(\text{CO})_3\}_2]$  and RNC ( $\text{L} = \text{Ph}_3\text{P}$  or  $\text{Bu}^n\text{P}$ ) were the salts  $[\text{L}_2\text{Co}(\text{CNR})_3][\text{Co}(\text{CO})_4]$  in which the cation has *trans* trigonal bipyramidal co-ordination about the cobalt atom.<sup>26</sup> In these reactions there was i.r. spectroscopic evidence for the formation of cations containing both carbonyl and isocyanide ligands.

The i.r. spectrum of  $[\{\text{Co}(\text{CO})_3(\text{CNMe})\}_2\text{Hg}]$  is more complicated than that of  $[\{\text{Et}_3\text{PCo}(\text{CO})_3\}_2\text{Hg}]$ <sup>27</sup> where it is known that there is trigonal bipyramidal co-ordination about each cobalt atom and that the P-Co-Hg-Co-P system is linear.<sup>28</sup> Therefore it is probable

that the methyl isocyanide ligands occupy at least one of the equatorial co-ordination positions of a  $[\{\text{Co}(\text{CO})_4\}_2\text{Hg}]$ -type of molecule.<sup>29</sup> It is probable that the linear P-Co-Hg-Co-P structure is retained in  $[\{\text{Ph}_3\text{P}\}_2\text{Co}(\text{CO})_2(\text{CNBu}^t)_2\text{Hg}]$  and the single absorption band due to its  $\nu(\text{CN})$  vibration implies a centrosymmetric molecule. The complexity of the i.r. spectrum of  $[\{\text{Bu}^n\text{P}\}_2\text{Co}(\text{CO})_3\text{Hg}\{\text{Co}(\text{CO})_2(\text{CNMe})(\text{PBu}^n)_3\}]$  suggests that isomers are present (*cf.*  $[\text{Co}_2(\text{CO})_5(\text{PMe}_3)_3\text{Hg}]$  in ref. 30).

The observed changes in the frequencies of the various absorption bands in the i.r. spectra of the compounds may be interpreted using the accepted model of the bonding between metal atoms and either carbonyl or isocyanide ligands. As RNC are weaker  $\pi$ -acceptors and/or stronger  $\sigma$ -donors than CO groups, replacement of the latter by the former causes a decrease in the frequency of both  $\nu(\text{CO})$  and  $\nu(\text{CN})$  vibrations.<sup>31</sup> The absolute frequencies of  $\nu(\text{CN})$  decrease along the series  $\text{R} = \text{Me} > n\text{-alkyl} > \text{sec-alkyl} > \text{tert-alkyl}$  and as the mass of R increases. The large band widths of these absorption bands, as compared with those due to  $\nu(\text{CO})$  modes, is also due to the presence of R. Similar behaviour is observed for absorption bands due to  $\nu(\text{CO})$  when the carbonyl group acts as Lewis base towards Lewis acids such as  $\text{BF}_3$ ,<sup>32</sup> or hydrogen bonds to alcohol solvents.<sup>33</sup>

An important feature of the properties of isocyanide ligands which has emerged in this work is their ability to stabilize polynuclear complexes. This is especially well illustrated by their reactions with octacarbonyldicobalt. Whereas phosphines, arsines, and stibines bring about a breakdown of this binuclear compound to salts, *e.g.*  $[(\text{Ph}_3\text{P})_2\text{Co}(\text{CO})_3][\text{Co}(\text{CO})_4]$ ,<sup>2</sup> under similar, mild conditions isocyanides cause a polymerisation to tetracobalt complexes. The almost total absence of  $[\text{Co}_4(\text{CO})_{11}(\text{CNR})]$  from such reactions even when very low concentrations of isocyanides are used suggest that  $[\text{Co}_2(\text{CO})_7(\text{CNR})]$  are formed first and rapidly dimerise to  $[\text{Co}_4(\text{CO})_{10}(\text{CNR})_2]$ .  $[\text{SCo}_3(\text{CO})_9]$  is the only compound which appears to be destabilized when its carbonyl ligands are replaced by RNC molecules. It has been suggested that in it the unpaired electron occupies a  $\sigma^*$  molecular orbital of the  $\text{SCo}_3$  framework.<sup>34</sup> If replacement of CO by CNR causes an increase in the energy separation between the  $\sigma$  and  $\sigma^*$  orbitals, *i.e.* stabilizes the former, then the behaviour of  $[\text{SCo}_3(\text{CO})_9]$  is not unexpected nor is it inconsistent with the other observations.

[4/344 Received, 21st February, 1974]

\* The i.r. spectrum of the orange crystals of  $[\text{MeCCo}_3(\text{CO})_6(\text{CNBu}^t)_3]$  as a Nujol mull shows absorption bands at 1800sh, 1834s, 1867w, 1967vs, 2004s, 2145s, and 2163m  $\text{cm}^{-1}$ .

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<sup>25</sup> K. Burger, L. Korecz, and G. Bor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1527.

<sup>26</sup> R. B. King and M. S. Saran, *Inorg. Chem.*, 1972, **11**, 2112.

<sup>27</sup> A. R. Manning, *J. Chem. Soc. (A)*, 1968, 1018.

<sup>28</sup> R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

<sup>29</sup> G. M. Sheldrake and R. N. F. Simpson, *J. Chem. Soc. (A)*, 1968, 1005.

<sup>30</sup> B. de Montauzon and R. Poilblanc, *J. Organometallic Chem.*, 1973, **54**, 291.

<sup>31</sup> P. M. Treichel, *Adv. Organometallic Chem.*, 1973, **11**, 21.

<sup>32</sup> A. Alich, N. J. Nelson, D. Stope, and D. F. Shriver, *Inorg. Chem.*, 1972, **11**, 2976.

<sup>33</sup> P. McArdle and A. R. Manning, *J. Chem. Soc. (A)*, 1970, 2123.

<sup>34</sup> C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229.