Tautomeric Equilibria in Solutions of $\{LCo(CO)_3\}_2$ Complexes (L = Tertiary Phosphine, Arsine, or Stibine)

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Studies of their i.r. spectra (1700—2100 cm^{-1}) show that solutions of various $\{LCo(CO)_3\}_2$ complexes $\{L = R_3M$, $R_2(R')M$, or p-$XC_6H_4(R)_2M$ (M = P, As, or Sb; R,R' = alkyl; and X = H, Me, MeO, Br, F, and CF_3 when R = Et$\}$ contain one non-bridged and two CO-bridged isomers. The first are favoured by higher temperatures, polar solvents, bulky ligands, and a higher electron density at the cobalt atom. These factors also affect the relative proportions of the two bridged tautomers which have been identified unequivocally.

SOLUTIONS of $\{(Et_3As)Co(CO)_3\}_2$ contain one non-bridged (nb) and two CO-bridged (b) isomers. Only the first is important for $\{(Et_3P)Co(CO)_3\}_2$.[1,†] In this present work we have identified unequivocally the bridged species, and have studied the effects of changes in solvent, temperature, and ligand (L) upon the isomer ratios in solution. We have attempted to separate the steric factors which determine the overall effect of a ligand from the electronic factors by investigating the complexes of some tertiary phosphines, a wide variety of tertiary arsines, and a few trialkylstibines.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen in purified solvents. Chemicals were purchased from the usual commercial sources. Tetraethyl-lead was a gift from Associated Octel Ltd.

Previously described methods, or modifications of them, were used to prepare Na_2O_3AsMe,[3] $MeAsI_2$,[4] $PhAsCl_2$,[5] Me_2AsI,[4] Et_2AsCl,[6] the various ligands, L,[7–11] and the $\{LCo(CO)_3\}_2$ complexes.[1] The yields of the last ranged from 5% [L = $(Pr^i)_3Sb$] to 80% [L = $Me(Pr^n)_2As$] but were generally *ca.* 55%. All were analytically pure (C, H, and Co).

I.r. spectra were obtained as described.[1] They are reported in Tables 1—4.

RESULTS

The stability of the red to brown $\{LCo(CO)_3\}_2$ complexes decreases for (*a*) L = $R_3P > R_3As > R_3Sb$ (*b*) for trialkylarsines containing two different alkyl groups, (*c*) with increasing alkyl chain length, and (*d*) on replacing an alkyl by an aryl group. We could not prepare complexes of $Ph_2(R)As$ or $Ph(R)_2Sb$ ligands.

TABLE 1

I.r. spectra (1700—2100 cm^{-1}) of some $\{LCo(CO)_3\}_2$ complexes in hexane solution at room temperature

L	Absorption bands [a] *A*	*B*	*C*	*D* [b]	*E*	*F*	*G*	*H* [b]	*I*	*J*
$Ph(Pr^i)_2P$				1959(10)				1975(1·8)		
Me_3P [c]	1757(vw)	1771(vw)	1785(vw)	1948(10)		1956(sh)		1967(vw)	1997(vw)	2032(vw)
Me_3As	1778(0·8)	1795(1·7)	1804(1·7)	1958(sh)	1966(sh)	1967(sh)	1971(6·8)	1982(4·0)	2004(10)	2035(2·5)
$Pr^n(Me)_2As$	1780(sh)	1794(2·4)	1804(2·2)	1957(sh)		1962(sh)	1970(7·3)	1976(5·9)	2003(10)	2035(2·4)
$Pr^i(Me)_2As$	1780(1·4)	1796(sh)	1804(2·4)	1956(5·3)		1959(sh)	1970(7·5)	1977(6·7)	2002(10)	2036(3·3)
$Pr^n_2(Me)As$	1779(1·0)	1793(1·8)	1804(1·6)	1956(4·6)	1958(sh)	1961(sh)	1968(6·1)	1977(4·6)	2002(10)	2034(2·4)
$Pr^i_2(Me)As$	1784(2·1)	1797(sh)	1804(2·0)	1954(22·5)	1957(sh)	1959(sh)	1969(5·1)	1976(8·7)	1999(10)	2034(2·4)
Et_3As	1780(1·5)	1793(1·6)	1805(1·8)	1953(14·9)	1957(sh)	1959(sh)	1968(5·8)	1974(6·1)	2000(10)	2032(2·5)
Pr^n_3As	1778(1·3)	1790(1·9)	1803(1·7)	1953(15·1)	1955(sh)	1957(sh)	1966(6·3)	1974(6·0)	1999(10)	2033(2·4)
Pr^i_3As				1952(10)				1973(1·3)		
Bu^n_3As	1780(1·4)	1789(1·7)	1803(1·9)	1954(14·3)	1957(sh)	1960(sh)	1967(6·2)	1975(6·2)	1999(10)	2033(2·6)
Bu^i_3As				1954(10)				1974(1·4)		
$(n\text{-Pentyl})_3As$	1780(1·3)	1790(1·3)	1803(1·7)	1953(18·3)	1955(sh)	1958(sh)	1966(5·6)	1974(6·7)	1999(10)	2033(2·7)
$(iso\text{-Pentyl})_3As$	1781(1·4)	1786(sh)	1803(1·6)	1953(23·7)	1956(sh)	1957(sh)	1965(4·6)	1974(6·9)	1999(10)	2032(3·1)
$(2\text{-Pentyl})_3As$				1951(10)				1971(1·4)		
$(n\text{-Octyl})_3As$	1780(1·5)	1788(1·7)	1802(1·9)	1954(18·7)	1958(sh)	1959(sh)	1965(5·7)	1974(6·5)	1999(10)	2033(2·8)
Et_3Sb	1791(sh)	1795(1·9)	1802(1·8)	1954(9·6)	1956(sh)		1967(6·8)	1974(sh)	2001(10)	2030(4·0)
Pr^i_3Sb				1952(10)				1971(1·1)		

[a] Peak positions with relative peak heights in parentheses. *G*, *I*, and *J* are usually doublets (*cf.* ref. 1). [b] Due to nb species. The b isomers are responsible for the remainder. [c] CS_2 solution. (vw) = Very weak, and (sh) = shoulder.

Although no compound has bridging carbonyl ligands in the solid state, in solutions of some there are one non-bridged (nb) and two CO-bridged species (b_l and b_h). These give rise to absorption band *D* and a component of *H*(nb), *B*, and *F* and components of *C*, *G*, *I*, and *J* (b_l), and *A* and components of *C*, *G*, *H*, *I*, and *J* (b_h) [*cf.* $\{Et_3AsCo(CO)_3\}_2$ in ref. 1].

Lowering the temperatures of solutions of some com-

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† Similar behaviour has been reported for $\{LCo_2(CO)_7\}$ (L = Et_3P or Et_3As).[2]

[1] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1665, and references therein.

[2] G. Bor, *Inorg. Chim. Acta* (Proc. First International Symposium Chem. Metal Carbonyls, Venice), 1968, F2.

[3] A. J. Quick and R. Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 811.

[4] H. Gilman and S. Avakian, *J. Amer. Chem. Soc.*, 1954, **76**, 4031.

[5] C. S. Hamilton and J. F. Morgan in ' Organic Reactions,' ed. R. Adams, Wiley, New York, 1944, vol. 2, p. 415.

[6] M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *J. Org. Chem.*, 1949, **14**, 429.

[7] W. C. Davies, *J. Chem. Soc.*, 1933, 1043.

[8] W. J. C. Dyke and W. J. Jones, *J. Chem. Soc.*, 1930, 2426.

[9] W. J. Jones, W. J. C. Dyke, G. Davies, D. C. Griffiths, and J. H. E. Webb, *J. Chem. Soc.*, 1932, 2284.

[10] W. J. C. Dyke, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 1930, 463.

[11] J. G. Evans, P. L. Goggin, R. J. Goodfellow, and J. G. Smith, *J. Chem. Soc.* (*A*), 1968, 464.

TABLE 2

The influence of temperature on the i.r. spectra (1700—2100 cm^{-1}) of some $\{LCo(CO)_3\}_2$ derivatives in iso-octane solution

Absorption bands [a]

Temperature (°C)	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
$\{Pr^n{}_2(Me)AsCO(CO)_3\}_2$										
20	1779(sh)	1793(1·8)	1804(1·6)	1956(4·6)	1958(sh)	1961(sh)	1968(6·1)	1977(4·6)	2002(10)	2034(2·4)
−77	1781(sh)	1790(2·9)	1803(1·7)	1955(sh)		1961(sh)	1967(7·8)	1977(2·4)	2002(10)	2034(3·3)
$\{Bu^n{}_3AsCo(CO)_3\}_2$										
20	1780(1·4)	1789(1·7)	1803(1·9)	1954(14·3)	1957(sh)	1960(sh)	1967(6·2)	1975(6·2)	1999(10)	2033(2·7)
−77	1779(sh)	1784(3·3)	1799(1·5)	1953(4·7)	1954(sh)	1960(sh)	1966(8·1)	1974(3·0)	1999(10)	2030(3·2)
$\{(Isopentyl)_3AsCo(CO)_3\}_2$										
20	1781(1·4)	1786(sh)	1803(1·6)	1953(23·7)	1956(sh)	1957(sh)	1965(4·6)	1974(6·9)	1999(10)	2032(3·1)
−77	1776(sh)	1783(2·6)	1800(1·2)	1952(10·1)	1953(sh)		1965(6·8)	1974(5·0)	1998(10)	2033(4·7)

[a] See *a* Table 1.

TABLE 3

The effect of solvent on the i.r. spectra (1700—2100 cm^{-1}) of some $\{LCo(CO)_3\}_2$ compounds at room temperature

Absorption bands [a]

Solvent [b]	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
$\{Pr^n(Me)_2AsCo(CO)_3\}_2$										
Hexane	1780(sh)	1794(2·4)	1804(2·2)	1957(sh)		1962(sh)	1970(7·3)	1976(5·9)	2003(10)	2035(2·4)
Xylene	1775(sh)	1787(3·8)	1798(2·9)	1950(9·6)			1965(9·1)	1971(sh)	1999(10)	2033(2·9)
THF	1773(sh)	1788(4·3)	1800(3·1)	1950(8·4)			1963(8·7)	1970(sh)	1997(10)	2030(2·6)
$\{Pr^i(Me)_2AsCo(CO)_3\}_2$										
Hexane	1780(1·4)	1796(sh)	1804(2·4)	1956(5·3)		1959(sh)	1970(7·5)	1977(6·7)	2002(10)	2036(3·3)
Xylene	1777(sh)	1787(2·5)	1796(2·5)	1949(15·7)			1964(8·6)	1971(sh)	1997(10)	2031(2·9)
THF		1788(2·3)	1794(sh)	1949(18·1)			1963(8·7)	1970(sh)	1997(10)	2030(2·6)
$\{(n\text{-}Pentyl)_3AsCo(CO)_3\}_2$										
Hexane	1780(1·3)	1790(1·3)	1803(1·7)	1953(18·3)	1955(sh)	1958(sh)	1966(5·6)	1974(6·7)	1999(10)	2033(2·7)
Xylene	1774(sh)	1780(2·5)	1798(1·9)	1948(60)			1956(sh)	1971(13·5)	1996(10)	2030(3·1)
THF	1774(sh)	1782(3·5)	1793(sh)	1947(66)			1956(sh)	1970(sh)	1993(10)	2029(3·3)
$\{(Isopentyl)_3AsCo(CO)_3\}_2$										
Hexane	1781(1·4)	1786(sh)	1803(1·6)	1953(23·7)	1956(sh)	1957(sh)	1965(4·6)	1974(6·9)	1999(10)	2032(3·1)
Xylene		1779(2·1)	1796(1·5)	1947(80)				1970(13·1)	1995(10)	2028(4·2)
THF	1773(sh)	1782(3·9)	1795(2·3)	1947(107)				1966(12·5)	1993(10)	2028(3·5)

[a] See footnote *a* in Table 1. [b] THF = Tetrahydrofuran.

TABLE 4

The i.r. spectra (1700—2100 cm^{-1}) of some $\{p\text{-}XC_6H_4(Et)_2AsCo(CO)_3\}_2$ and related complexes in hexane solution at room temperature

Absorption bands [a]

Ligand	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
$C_6H_5(Me)_2As$	1787(sh)	1800(1·6)	1812(sh)	1962(sh)		1968(sh)	1979(5·0)		2008(10)	2038(3·1)
Me_3As	1778(0·7)	1795(1·7)	1804(1·7)	1958(sh)	1966(sh)	1967(sh)	1971(6·8)	1982(4·0)	2004(10)	2035(2·5)
$p\text{-}CF_3C_6H_4(Et)_2As$	1784(sh)	1794(2·0)	1803(sh)	1961(8·5)	1963(sh)	1965(sh)	1976(sh)	1982(5·9)	2008(10)	2037(3·0)
$p\text{-}BrC_6H_4(Et)_2As$	1785(sh)	1796(1·8)	1807(1·5)	1960(9·4)	1962(sh)	1964(sh)	1975(sh)	1981(6·3)	2006(10)	2037(3·0)
$Ph(Et)_2As$	1783(sh)	1795(1·6)	1805(sh)	1960(11·1)	1964(sh)	1969(sh)	1975(sh)	1980(6·4)	2006(10)	2037(2·6)
$p\text{-}FC_6H_4(Et)_2As$	1787(sh)	1796(1·5)	1806(sh)	1960(11·4)	1963(sh)	1966(sh)	1975(sh)	1981(6·5)	2006(10)	2036(2·6)
$p\text{-}MeC_6H_4(Et)_2As$	1785(sh)	1796(1·6)	1805(sh)	1958(13·6)	1961(sh)	1963(sh)	1973(sh)	1978(7·8)	2003(10)	2034(2·8)
$p\text{-}MeOC_6H_4(Et)_2As$	1784(sh)	1793(2·0)	1803(1·6)	1957(17·6)	1960(sh)	1963(sh)	1972(sh)	1978(7·8)	2003(10)	2034(2·7)
Et_3As	1780(1·5)	1793(1·6)	1805(1·8)	1953(14·9)	1957(sh)	1959(sh)	1968(5·8)	1974(6·1)	2000(10)	2034(2·5)
$PhCH_2(Et)_2As$	1775(sh)	1788(1·7)	1806(2·0)	1957(17·5)	1960(sh)	1962(sh)	1969(6·9)	1977(7·3)	2003(10)	2034(3·1)
$Ph(Bu^s)_2As$				1957(10)				1977(2·2)		
$Ph(Bu^i)_2As$				1958(10)				1979(1·8)		
$Ph(Isopentyl)_2As$	1783(sh)	1793(1·8)	1805(1·7)	1958(11·2)	1961(sh)	1963(sh)	1972(sh)	1979(7·8)	2003(10)	2035(2·9)
$(Isopentyl)_3As$	1781(1·4)	1788(1·1)	1803(1·6)	1953(23·7)	1956(sh)	1957(sh)	1965(4·6)	1974(6·9)	1998(10)	2032(3·1)

[a] See footnote *a* in Table 1.

pounds causes the proportions of the b isomer to increase at the expense of the nb forms as measured by the intensity ratios of $(A + B) : D$ or $I : D$. At the same time the changes in the intensity ratios $B : A$ imply that at *ca.* −80 °C, the low temperature (b_l) isomers predominate to the virtual exclusion of the high temperature (b_h) isomers (Table 2).

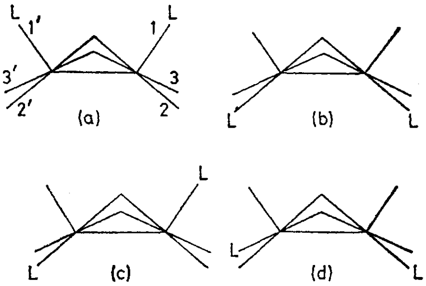
Varying the solvent along the series heptane, carbon disulphide, xylene, tetrahydrofuran brings about increases in the concentration ratios $(b_l) : (b_t)$ and $(nb) : \{(b_l) + (b_t)\}$. Typical results are shown (Table 3).

The proportions of the nb increase at the expense of the b forms along the series (a) $L = R_3Sb < R_3As < R_3P$, (b) $R = Me < Et \sim Pr^n \sim Bu^n <$ n-pentyl $\sim$ n-octyl $<$ isopentyl $<$ isobutyl $<$ s-alkyl, (c) $L = Me_3As < Me_2(Pr^n)As < Me(Pr^n)_2As < Me_2(Pr^i)As < Pr^n{}_3As < Me(Pr^i)_2As < Pr^i{}_3As$, (d) $L = Ph(R)_2As < R_3As$ for R = Et and isopentyl, and (e) $X = CF_3 < Br < F \sim H < Me < MeO$ for $L = p\text{-}XC_6H_4(Et)_2As$ (Table 4). Where bridged tautomers are observed, the concentration ratio $(b_h) : (b_l)$ increases along the series (a), (b), and (d), and also for $L = Me_3As < Me_2(Pr^n)As < Me(Pr^n)_2As < Pr^n{}_3As < Me_2(Pr^i)As < Me(Pr^i)_2As$.

DISCUSSION

The tautomerism first observed for $\{(Et_3As)Co(CO)_3\}_2$[1] is common. Although the original suggestion that the nb species have D_{3d} symmetry is probably correct (it appears to be the only form found in the solid state [12]), the identification of the two b tautomers as 2,2′- and 2,3′-isomers (Figure) is not consistent with other evidence.[13-16]

The separation of *A* and *C* is *ca.* 25 cm^{-1} as compared with *ca.* 45 cm^{-1} observed [13,14] for the two $\nu(CO\mu)$ absorption bands of $[\{\overline{CF_2(Me_2As)C{=}C(AsMe_2)CF_2}\}Co_2(CO)_6]$ which is a 2,2′-isomer.[13,15] By a process of elimination, the b_h tautomers must be 1,2′-isomers (Figure) where the two μ-CO ligands are in different environments.



The possible isomers of a CO-bridged $\{LCo(CO)_3\}_2$ complex; (a) 1,1′-, (b) 2,2′-, (c) 1,2′-, and (d) 2,3′-. The numbering of the terminal co-ordination positions are given on (a). CO ligands and Co atoms have been omitted for clarity

In the b_l-forms, the two μ-CO ligands are in similar environments. These isomers are virtually the sole species present at *ca.* −80° in solutions of *e.g.* $\{Me_2(Pr^n)AsCo(CO)_3\}_2$ in iso-octane. Their spectra (1700—2100 cm^{-1}) are almost identical with that of 2,3′-$\{1,6\text{-}Me_2As(CH_2)_6AsMe_2\}Co_2(CO)_6$.[16] Thus they are identified as 2,3′-isomers (Figure).

The absence of an absorption band at *ca.* 2058 cm^{-1} (*cf.* 1,1′-$[\{Ph_2AsCH_2CH_2AsPh_2\}Co_2(CO)_6]$[16]) or one at *ca.* 1830 cm^{-1} (*cf.* 2,2′-$[\{1,4\text{-}Me_2As(CH_2)_4AsMe_2\}Co_2(CO)_6]$ [16]) in any spectra show that 1,1′- and 2,2′-tautomers are not present in any solution of the $\{LCo(CO)_3\}_2$ complexes.

Many features of the equilibria may be rationalised on the basis that the compounds will attempt to minimise the steric interactions between ligands, especially those co-ordinated to different metal atoms. We have assumed (*a*) that the various isomers have the same geometries as octacarbonyldicobalt,[17] and (*b*) that trends in the changes of the relative intensities of absorption bands is a reasonably accurate reflection of changes in the relative concentrations of isomers. The structure of 2,2′-$[\{CF_2(Me_2As)C{=}C(AsMe)_2CF_2\}Co_2(CO)_6]$ [13,15] shows that (*a*) is reasonable, whilst other observations [18,19] imply that (*b*) is probably valid for a series of such closely related complexes as those described here.

The short inter-ligand separation and the relative directions of the Co–As bonds in both the 1,1′- and 2,2′-isomers would clearly lead to large repulsions between the two adjacent arsine ligands. Consequently, complexes of unidentate ligands adopt exclusively the 1,2′- and 2,3′-structures where such repulsions must be virtually non-existent.

The relative concentrations of the 1,2′- and 2,3′-isomers may be related to the repulsions between the tertiary arsines and the ' adjacent ' CO groups co-ordinated to the other cobalt atom. The separation of any two ligands in the 1 and 1′ positions will be greater than if they occupied the 2 and 2′.[17] Therefore, ' adjacent ' interactions would increase more rapidly for the 2,3′(b_l)- than the 1,2′(b_h)-isomers as the bulk of trialkylarsine ligand is increased, and cause the b_l/b_h equilibria to shift towards the latter. At the same time, both CO-bridged isomers are destabilized with respect to the non-bridged where there are no ' adjacent ' interactions and where *cis*-interactions between ligands co-ordinated to the same metal atom are probably no larger than in the bridged tautomers. The bulk of the arsine may be increased either by the branching of R, *e.g.* in $\{R_3AsCo(CO)_3\}_2$ complexes, or by introducing more branched alkyl groups onto the arsenic atom, *e.g.* in $\{Me_n(R')_{3-n}AsCo(CO)_3\}_2$ derivatives ($R' = Pr^n$ or Pr^i; and $n = 3$—0).

Arguments based on electronic effects are not satisfactory. They cannot explain the large energy difference between the 1,1′- and 2,2′-forms, and the 1,2′- and 2,3′-isomers, which is implied by the total absence of the first pair. Furthermore, the electronic consequences of replacing a β-hydrogen atom in $\{R_3AsCo(CO)_3\}_2$ by a methyl group when $R = Et$ and when $R = Pr^n$ must be virtually identical. Yet the insignificant effect of the first contrasts with the drastic destabilization of the b forms brought about by the second.

However, two observations require that electronic factors be considered. Replacing R_3As ligands by $Ph(R)_2As$ (R = Et or isopentyl) brings about a marked increase in the [b]/[nb] concentration ratio. Also, a dramatic change results from replacing arsines by phosphines or stibines. This is unlikely to be due entirely to the relatively small increase in the bulk of R_3M ligands for $M = Sb < As < P$.[†,20]

[†] The effective bulk of a R_3M ligand is due primarily to the groups R. It will decrease as the size of M increases and increases the R–Co separation.

[12] J. A. Ibers, *J. Organometallic Chem.*, 1968, **14**, 423; and R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

[13] J. P. Crow, W. R. Cullen, W. Harrison, and J. Trotter, *J. Amer. Chem. Soc.*, 1970, **92**, 6339.

[14] J. P. Crow and W. R. Cullen, *Inorg. Chem.*, 1971, **10**, 2165.

[15] W. Harrison and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1607.

[16] D. J. Thornhill and A. R. Manning, *J.C.S. Dalton*, 1973, 2086.

[17] G. C. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

[18] K. Noack, *Helv. Chim. Acta*, 1962, **65**, 1847.

[19] J. G. Bullitt and F. A. Cotton, *Inorg. Chim. Acta*, 1971, **5**, 637.

[20] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

To investigate the effects of electronic factors on the b/nb equilibria, we have prepared a series of $\{p\text{-XC}_6\text{H}_4(\text{Et})_2\text{AsCo(CO)}_3\}_2$ complexes, and have found that the nb forms increase in importance along the series $\text{X} = \text{CF}_3 < \text{Br} < \text{F} \sim \text{H} < \text{CH}_3 < \text{MeO}$. This is unlikely to be due to the steric effects of X, but it correlates well with the total electron-withdrawing capacity of the *para*-substituent as measured by the Taft coefficients σ_p which decrease for $\text{X} = \text{CF}_3 > \text{Br} > \text{F} > \text{H} > \text{Me} > \text{MeO}$.[21] As independent experimental evidence has related properties, *e.g.* basicity and nucleophilicity, of R_3M ligands (M = N, P, As, and Sb) to the nature of R,[22-29] it is not unreasonable to assume that X influences the electron density at the metal atom to which the $p\text{-XC}_6\text{H}_4(\text{Et})_2\text{As}$ ligands are co-ordinated.

Thus an increase in electron density at the metal atoms due to changes in L appears to favour the non-bridged isomers at the expense of the bridged, which implies that a μ-CO group is a better σ-donor and/or poorer π-acceptor than a terminal ligand. This is consistent with the effects of changes of $\text{L} = \text{R}_3\text{P} < \text{R}_3\text{As} < \text{R}_3\text{Sb}$, $\text{L} = \text{Et}_3\text{As} < \text{Ph(Et)}_2\text{As}$, and $\text{L} = \text{PhCH}_2(\text{Et})_2\text{As} < \text{Et}_3\text{As}$. Stibines are known to transfer less electron density to metal atoms than phosphines,[30,31] the phenyl group is more electron withdrawing than the ethyl, and the known stability of the benzyl cation may well cause a polarisation $\text{PhCH}_2(\delta+)\text{-As}(\delta-)$, but this may also be a steric effect.

Electronic factors also appear to influence the $\{\text{b}_l\}/\{\text{b}_h\}$ concentration ratio [*cf.* $\{\text{Et}_3\text{AsCo(CO)}_3\}_2$ and $\{\text{Ph(Et)}_2\text{AsCo(CO)}_3\}_2$]. We were not able to investigate this further due to the low stability of the $\{p\text{-XC}_6\text{H}_4(\text{Et})_2\text{AsCo(CO)}_3\}_2$ derivatives.

Changes in solvent effect all equilibria for $\{\text{LCo(CO)}_3\}_2$ complexes. However the nb tautomers are favoured by increasing solvent polarity, whereas with $\{(\pi\text{-dienyl})\text{Ru(CO)}_2\}_2$ (dienyl = C_5H_5 or MeC_5H_4) such a change favours the b isomers.[32]

At higher temperatures, the equilibria shift towards the nb forms. Similar behaviour has been reported for $\text{Co}_2(\text{CO})_8$,[33] $\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2$,[34] $\{(\pi\text{-dienyl})\text{Ru(CO)}_2\}_2$,[32,35] and $\{(\pi\text{-dienyl})\text{FeCo(CO)}_6\}$ (dienyl = C_5H_5, MeC_5H_4, and C_9H_7).[36]

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[21] R. W. Taft in ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13, p. 556.

[22] W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1937, 1622.

[23] W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, 1960, **82**, 5791.

[24] W. C. Davies and W. P. G. Lewis, *J. Chem. Soc.*, 1934, 1599.

[25] W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, 1960, **82**, 5794.

[26] R. R. Shagidullin, B. D. Chernakol'skii, I. A. Lamanova, A. S. Gel'fond, and G. Kh. Kamai, *Izvest. Akad. Nauk. S.S.R. Ser. Khim.*, 1969, 1490; *J. Organometallic Chem. Rev.*, 1970, **6***B*, 573.

[27] B. D. Chernakol'skii, A. S. Gel'fond, and G. Kh. Kamai, *Zhur. Obsch. Khim.*, 1969, **39**, 829; *J. Organometallic Chem. Rev.*, 1970, **6***B*, 573.

[28] C. N. R. Rao, J. Ramachandran, and A. Bulasubramanian, *Canad. J. Chem.*, 1961, **39**, 171.

[29] E. N. Tsvetkov, D. I. Labanov, G. Kh. Kamai, N. A. Chodaeva, and M. I. Kabachnik, *Zhur. Obschei. Khim.*, 1969, **39**, 2670; *J. Organometallic Chem. Rev.*, 1971, **8***B*, 188.

[30] C. Barbeau and J. Turcote, *Canad. J. Chem.*, 1970, **48**, 3583.

[31] G. Piazza, A. Foffani, and G. Poliani, *Z. phys. Chem.*, 1968, **60**, 177.

[32] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2128, and references therein.

[33] K. Noack, *Spectrochim. Acta*, 1963, **19**, 1925; *Helv. Chim. Acta*, 1964, **47**, 1555.

[34] K. Noack, *J. Organometallic Chem.*, 1967, **7**, 151.

[35] R. D. Fischer, A. Vogler, and K. Noack, *J. Organometallic Chem.*, 1967, **7**, 135.

[36] A. R. Manning, *J. Chem. Soc.* (*A*), 1971, 2321.