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SYNTHESIS AND FRAGMENTATION KINETICS OF TETRAKIS(TRIPHENYLPHOSPHINE)OCTACARBONYLTETRACOBALT

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Summary

Reaction of $Co_4(CO)_{12}$ with triphenylphosphine is shown to proceed at room temperature in n-heptane or 1,2-dichloroethane (DCE) to form $Co_4(CO)_8(PPh_3)_4$ which has been isolated and characterized by analysis and IR spectroscopy. The complex is rather unstable to air and light, especially in solution Its IR spectra show that $Co_4(CO)_8(PPh_3)_4$ probably exists as an equilibrium mixture of forms containing symmetrically bridging and semibridging CO groups, the form with semibridging carbonyls being favored by steric effects and by DCE as a solvent as compared to n-heptane. The kinetics of fragmentation in DCE to form $Co_2(CO)_6(PPh_3)_2$ have been studied and shown to proceed by three paths that involve, in order of decreasing ease, rate-determining PPh_3 dissociation, CO dissociation, and spontaneous activation without loss or gain of ligands in forming the transition state. The activation parameters for spontaneous fragmentation suggest that the degree of weakening of the bonding within the Co_4 cluster is quite high in the transition state and that the Co_4 cluster is weaker than the Ru_3 cluster in $Ru_3(CO)_9(PPh_3)_3$ The complexes $Co_4(CO)_8\{P(OMe)_3\}_4$, $Co_4(CO)_8(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$), and probably $Co_4(CO)_8(P\text{-}n\text{-}Bu_3)_4$ are shown to be much more stable to fragmentation than $Co_4(CO)_8(PPh_3)_4$ and the instability of the latter is ascribed to the steric effect of its large substituents.

Substitution of one carbonyl group in dodecacarbonyl tetracobalt is well known to be very facile and several monosubstituted derivatives have been isolated [1]. Di- and tri-substituted complexes are also known for several ligands but the only tetrasubstituted $Co_4(CO)_8L_4$ complexes that have been isolated are with the phosphites $P(OPh)_3$ [2], $P(OMe)_3$ [3], and $P(OCH_2)_3CEt$ [3]. It was suggested [3] that the more basic trialkylphosphines cause ready fragmentation of the Co_4 cluster and that, on the other hand, the inability to isolate $Co_4(CO)_8(PPh_3)_4$ arises from the "excessively low solubility of the bi-product $Co_2(CO)_6(PPh_3)_2$" [3]. We report here the isolation of $Co_4(CO)_8(PPh_3)_4$ and a study of the kinetics

0022-328X/82/0000—0000/$02 75

of its fragmentation reactions together with some observations on the stability towards substitution and fragmentation of some other Co_4 clusters.

Experimental

Materials

$Co_4(CO)_{12}$ (Strem Chemicals, Inc.) was used as received and stored under nitrogen in a refrigerator. Triphenylphosphine (BDH Laboratory Reagent), triphenylarsine (Eastman Kodak Co.), trimethylphosphite and dppm (Strem Chemicals, Inc.), and tri-n-butylphosphine (Baker Chemical Co.) were used as received. Dichloroethane, DCE (Baker Analyzed) and n-heptane (Aldrich Chemical Co., Spectroscopic Grade) were dried over molecular sieves. N_2 (Prepurified) and carbon monoxide (C.P. Grade, 99.5%) were obtained from Union Carbide of Canada, Ltd.

Procedures

Stock solutions of $Co_4(CO)_{12}$ were prepared by weighing under N_2 and dissolving in degassed solvent in the dark. The solutions were then further degassed in a foil-wrapped Schlenk tube by at least three freeze-pump-thaw cycles and stored in a refrigerator under an atmosphere of CO. Such solutions are stable for several weeks. Stock solutions of P-donor ligands were also prepared by weighing, degassed by several freeze-pump-thaw cycles, and stored under N_2 Reactions were initiated by mixing solutions in Schlenk tubes under an inert atmosphere. Transfers were made by means of syringes with stainless steel needles that were inserted through the rubber septum caps sealing the Schlenk tubes Samples for spectroscopic analysis were expelled through stainless steel tubes by a positive pressure of inert gas. All manipulations were carried out in very dim light. Spectra were measured in 1 mm path-length cells in Perkin Elmer 257 and 267 spectrophotometers

Kinetics were followed by spectroscopic measurement of samples expelled at regular intervals from solutions in Schlenk tubes immersed in a thermostatted glycol bath.

Results

The IR spectrum of a 1×10^{-3} *M* solution of $Co_4(CO)_{12}$ in n-heptane was in excellent agreement with that reported for solutions in hexadecane (Table 1) The spectrum in DCE was essentially the same but all the bands were slightly broader and the peak at 2035 cm^{-1} was not resolved. The other three bands had essentially the same relative intensities in n-heptane and DCE

Formation of $Co_4(CO)_{11}L$ *(L =* PPh_3, $AsPh_3$, $P(OMe)_3$, $P\text{-}n\text{-}Bu_3$*)*

Reactions of 1×10^{-3} *M* $Co_4(CO)_{12}$ with 5- to 10-fold excesses of the monodentate ligands L in n-heptane led immediately to $Co_4(CO)_{11}L$ as indicated by the IR spectra. The spectrum of $Co_4(CO)_{11}(PPh_3)$ is shown in Table 1 but the spectra of the other complexes are very similar. In DCE further reaction was more rapid and the monosubstituted complexes were only observable when $L = PPh_3$ and $AsPh_3$ and $[L] \leq 0.005$ *M*, the spectra being closely similar to those in n-heptane.

Further reaction of $Co_4(CO)_{11}(PPh_3)$ with PPh_3

Reactions in n-heptane continued over a period of 15—20 min at room temperature after which the spectra remained constant for an extended period Reaction in DCE was somewhat faster but in both solvents the rates increased with increasing [PPh_3]

The product of reaction of DCE solutions ca 5×10^{-3} *M* in $Co_4(CO)_{12}$ and 2.4×10^{-2} *M* in PPh_3 was isolated after 15 min at room temperature by removal of the solvent with bubbling argon. The small excess of PPh_3 was removed by washing with cold cyclohexane in which the product complex is only slightly soluble. The final residue was then reprecipitated from benzene-pentane as a reddish-brown powder in virtually quantitative yield. Anal. Calc. for $Co_4(CO)_8\{P(C_6H_5)_3\}_4$: Co, 15 62, C, 63 68; H, 4.00, P, 8.21%. Found. Co, 15 8, C, 62 5, H, 4.4, P, 8 2%. IR spectra of the product are shown in Fig 1 Residues after reaction in n-heptane and removal of solvent with bubbling argon gave the same IR spectra as those produced from reaction in DCE

The nature of the product in DCE was further examined by measurement of the IR spectra of solutions of $Co_4(CO)_{12}$ which had been allowed to react to completion with various amounts of PPh_3 The intensity of the bands due

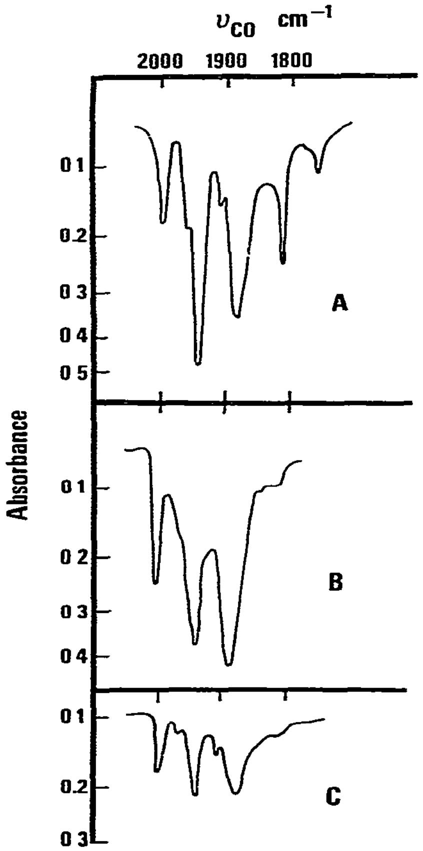

Fig 1 IR spectra of $Co_4(CO)_8(PPh_3)_4$ A in n-heptane B in DCE C in suspension in Nujol

TABLE 1

IR SPECTRA OF $Co_4(CO)_{12}$ AND SOME RELATED CLUSTERS

Complex	Solvent	ν(CO) (cm^{-1})			
$Co_4(CO)_{12}$	n-heptane	2013vw	2060vs	2050vs	2045
$Co_4(CO)_{12}$	DCE	2110vw	2060vs	2050vs	2040
$Co_4(CO)_{12}$	hexadecane	2105vw	2063vs	2054vs	2047
$Co_4(CO)_{11}(PPh_3)$ [a]	n-heptane	2090s	2050s(sh)	2043vs	2035
$Co_4(CO)_{11}(PPh_3)$ [a]	DCE	2085s	2050s(sh)	2042vs	2030
$Co_4(CO)_{11}(PPh_3)$	n-heptane	2084s	2045vs	2039vs	2030
$Ir_4(CO)_{11}(PPh_3)$	CHCl3	2090	2058		2023
$Co_4(CO)_9(PEt_3)_3$	hexadecane	2036w	2025m	1992m	1978
$Co_4(CO)_9(P\text{-}n\text{-}Bu_3)_3$ [a]	n-heptane	2030w		1990(sh)	1980
$Ir_4(CO)_9(P\text{-}n\text{-}Bu_3)_3$	paraffins	2033m		2010w	1990
$Co_4(CO)_8(dppm)_2$ [a]	DCE			2014m	1972
$Co_4(CO)_8(dppm)_2$	CS_2	2070w		2016s	1975
$Rh_4(CO)_8(dppm)_2$	CS_2	2066m(br)		2026s	1966
$Co_4(CO)_8(PPh_3)_4$	Nujol			2005s	1972
$Co_4(CO)_8(PPh_3)_4$	n-heptane			2005m	1965
$Co_4(CO)_8(PPh_3)_4$	DCE			2010s	1970
$Co_4(CO)_9(PPhMe_2)_3$	hexadecane			2037m	2029
$Co_4(CO)_8\{P(OMe)_3\}_4$ [a]	n-heptane			2016m	1972
$Co_4(CO)_8\{P(OMe)_3\}_4$ [a]	DCE				1975
$Co_4(CO)_8\{P(OMe)_3\}_4$	hexadecane			2018m	1980

[a] Prepared in situ in the presence of excess ligand

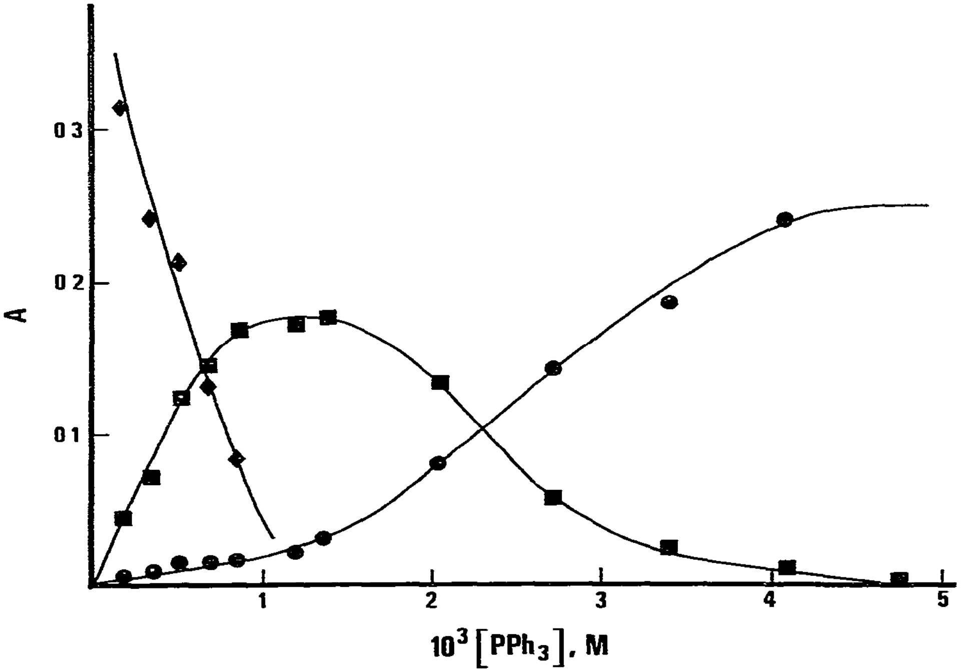

Fig 2 Dependence on $[PPh_3]$ of the absorbance of IR bands at 2050 cm^{-1} (◆) due to $Co_4(CO)_{12}$ 2085 cm^{-1} (■) due to $Co_4(CO)_{11}(PPh_3)$ and 1950 cm^{-1} (●) due to $Co_4(CO)_8(PPh_3)_4$ after reaction of ca $1 \times 10^{-3}\,M$ solutions of $Co_4(CO)_{12}$ in DCE with PPh_3

					Ref
		1896vw	1864s	1830vw	This work
ı)		1896w	1860m		This work
	2027w	1898w	1864w		3
	1853m	1835m			This work
	1850m	1830m			This work
	1855m	1838m			1
	1846	1823			15
ı)	1957w	1940w		1780m	3
	1955vs	1910m	1808w	1775s	This work
	1960m			1780s(br)	8
ı)	1890w		1825(sh)	1775m	This work
	1890w		1830w	1780m(br)	This work
			1818m	1792m	6
	1912w	1882s(br)	1810w		This work
	1910w	1885s(br)	1810m	1755w	This work
		1890s(br)	1820w	1765w	This work
	1979vs	1960m	1805m	1786s	3
				1792m	This work
sh)		1910w(sh)		1810m	This work
				1792s	3

to $Co_4(CO)_{11}(PPh_3)$ grew to a maximum with increasing $[PPh_3]$ and then decreased as bands due to the final product grew. As is shown in Fig. 2, slightly more than four times as much PPh_3 was required to reduce the intensity of the $Co_4(CO)_{11}(PPh_3)$ bands to zero as was required to form $Co_4(CO)_{11}(PPh_3)$ in the absence of appreciable bands due to $Co_4(CO)_{12}$ or product. The spectra of the solutions remained unchanged in the presence of larger amounts of PPh_3 at room temperature. However, when the temperature was raised to $\geq 40°C$, further spectroscopic changes occurred and eventually a reddish-brown precipitate formed The spectroscopic changes involved almost complete loss of the bands at 2010 cm^{-1} and 1890 cm^{-1} and a growth of the band at 1950 cm^{-1} until precipitation began to occur When the precipitate was separated and dissolved in heptane the IR spectrum showed a single strong band at 1950 cm^{-1} characteristic of $Co_2(CO)_6(PPh_3)_2$.

The product of the room-temperature reaction was quite unstable to light and air in solution and attempts to measure its molecular weight by osmometry in chloroform at 38°C were vitiated by extensive decomposition. Thoroughly deoxygenated solutions of the product in DCE under argon showed no evidence of any ESR signals even at maximum instrument sensitivity. The molecular weight of $Co_4(CO)_8(PPh_3)_4$ is too high for the parent ion to be detectable on the mass spectrometers available to us.

Further reaction of $Co_4(CO)_{11}L$ with L ($L = AsPh_3$, $P(OMe)_3$, and P-n-Bu_3)

No further reaction of $Co_4(CO)_{11}(AsPh_3)$ with a 10-fold excess of $AsPh_3$ in DCE was observed even after 75 min at room temperature and a further 2 h at

45°C Reaction of $Co_4(CO)_{11}\{P(OMe)_3\}$ with a 10-fold excess of $P(OMe)_3$ in n-heptane at room temperature over a period of 30 min led to $Co_4(CO)_{10}\{P(OMe)_3\}_2$ as shown by the changes in the IR spectra [3,4]. $Co_4(CO)_9\{P(OMe)_3\}_3$ was formed completely after a further 20 min at 60°C, and $Co_4(CO)_8\{P(OMe)_3\}_4$ after a further 3 h at 65°C No changes in the IR spectra occurred subsequently, even at 65°C over a period of 2 h. In DCE reaction for only 10 min at room temperature was required to form $Co_4(CO)_{10}\{P(OMe)_3\}_2$ completely. A further 2 h at 40°C was sufficient to form $Co_4(CO)_9\{P(OMe)_3\}_3$ and a further 3 h at 65°C produced $Co_4(CO)_8\{P(OMe)_3\}_4$

After the immediate formation of $Co_4(CO)_{11}(PBu_3)$, on reaction of $Co_4(CO)_{12}$ with a 7-fold excess of PBu_3, a further reaction occurred at room temperature over a period of 40 min to form a product whose spectrum (Table 1) closely resembled those of $Co_4(CO)_9(PEt_3)_3$ [3] and $Ir_4(CO)_9(PBu_3)_3$ [8]. This is presumably $Co_4(CO)_9(PBu_3)_3$. Further reaction required the temperature to be raised to 60—80°C when a complex series of spectroscopic changes ensued No spectral bands characteristic of $Co_2(CO)_6(PBu_3)_2$ or more highly substituted dicobalt carbonyls [5] were observed

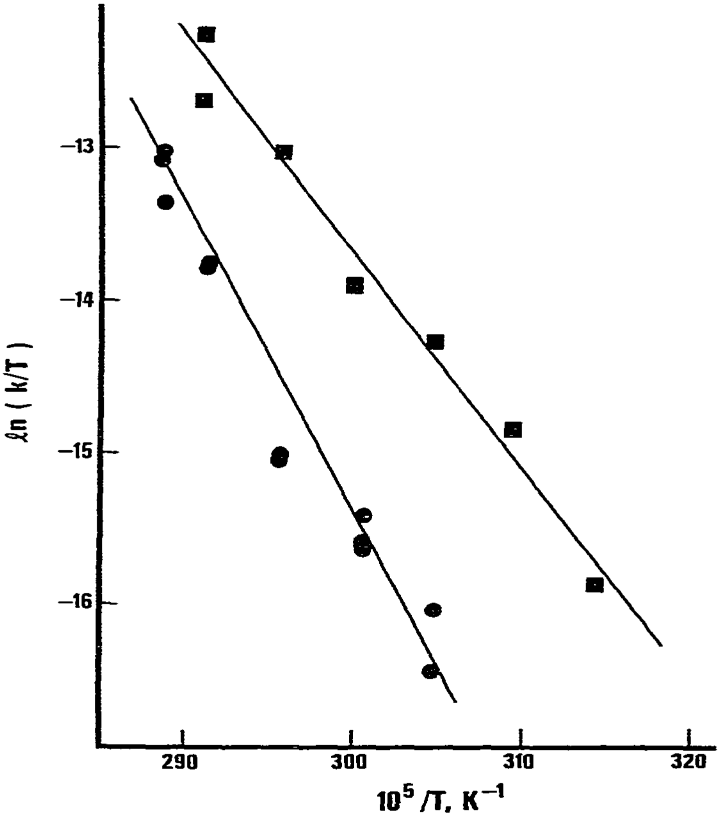

Fig 3 ● Temperature dependence of $\ln(k_{obs}/T)$ for the [CO]- and [PPh_3]-independent fragmentation of $Co_4(CO)_8(PPh_3)_4$ in DCE. ■. Temperature dependence of 0 5 + $\ln(k/T)$ for the fragmentation of $Co_4(CO)_8(PPh_3)_4$ by the CO-dissociative path. $k = k_{obs}$ for [PPh_3]-independent reaction under N_2 minus k_{calc} for the [CO]- and [PPh_3]-independent reaction

Reaction of $Co_4(CO)_{12}$ with $Ph_2PCH_2PPh_2$

Reaction of $Co_4(CO)_{12}$ with dppm ($Ph_2PCH_2PPh_2$) in DCE at room temperature led within 40 min to a product with an IR spectrum (Table 1) very like that of $Rh_4(CO)_8(dppm)_2$ in CS_2 [6]. Evaporation of the solvent and reprecipi-

TABLE 2

RATE PARAMETERS FOR THE REACTION $Co_4(CO)_8(PPh_3)_4 \xrightarrow{PPh_3} Co_2(CO)_6(PPh_3)_2$ IN DICHLOROETHANE [COMPLEX] = 1—2 × 10^{-3} *M*

T(°C)	10^3[PPh_3] (*M*)	p(CO) (%) [a]	$10^6 k_{obs}$ (s^{-1})
45.0	62.0	0	30.1
50.0	62.0		83.8
55.0	62.0		159
59.5	9.5		465
	19.0		395
	32.0		178
	50.0		114
	50.0	5.3	83.2
		25.4	71.5
		40.9	59.5
		100	61.3
	76.0	0	140
	81.0		137
	105		147
	152		156
60.0	62.0		252
65.0	62.0		601
70.0	62.0		966 1310
55.0	40.0	100	24.0
	60.0		36.4
59.5	14.0		111
	15.0		80.9
	22.0		71.2
	36.0		56.9
	40.0		55.3
	60.0		58.4
	120		53.9
	201		69.5
65.0	40.0		101
	50.0		105
	60.0		102
70.0	40.0		366
	60.0		359
75.0	30.0		559
	40.0		563
	50.0		729
	60.0		779

For CO dissociative path [b] *(see Discussion)*

$\Delta H^{\ddagger}$ = 28.3 ± 1.0 [c d] kcal mol^{-1} $\Delta S^{\ddagger}$ = 9.5 ± 5.6 [c, d] cal K^{-1} mol^{-1}

For spontaneous fragmentation [c] *(see Discussion)*

$\Delta H^{\ddagger}$ = 35.1 ± 1.6 [d] kcal mol^{-1} $\Delta S^{\ddagger}$ = 27.3 ± 4.6 [d] cal K^{-1} mol^{-1}.

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[a] Mol % CO in CO-N_2 mixtures. [b] These parameters were estimated by subtracting the rate constants calculated from the least squares parameters for the spontaneous fragmentation reaction from the rate constants obtained under N_2 with [PPh_3] = 0.062 *M* [c] The errors are estimates of the standard deviations based on the internal consistency of the data and do not include any contribution from the uncertainty in the calculated values of the rate constants for spontaneous fragmentation. [d] These estimates of the standard deviations arise from the scatter of the data around the values calculated from the least squares parameters and in both cases the values of $[\Sigma \{(k_{obs} - k_{calc})/k_{calc}\}^2/(N-2)]^{1/2}$ are ca. 20% where N = number of values of k_{obs} used.

tation of the orange-brown product from benzene-pentane solutions gave a complex with an IR spectrum in CS_2 that was essentially the same as that found at the end of reaction in DCE but with better resolved bands The IR spectrum of the product formed in situ in DCE remained unchanged after 4 h at 65°C

Kinetics of fragmentation of $Co_4(CO)_8(PPh_3)_4$

The kinetics of fragmentation of $Co_4(CO)_8(PPh_3)_4$ to form $Co_2(CO)_6(PPh_3)_2$ were followed by monitoring the decreasing absorbance of the IR band at 2010 cm^{-1} Although the product was not completely soluble in DCE its precipitation did not generally become noticeable until the reaction was 60—70% complete. Reaction in n-heptane was not convenient for kinetic study because precipitation of $Co_2(CO)_6(PPh_3)_2$ occurred much earlier. First order rate plots were usually linear for up to 2 half lives when $[PPh_3] <$ ca. 0.2 M At higher values of $[PPh_3]$ solutions turned green towards the end of the reaction, the rate plots obtained were linear for only 1 half life, and the rate constants were of poor reproducibility. The rate data are shown in Table 2. At the fairly high values of $[PPh_3]$ used in these kinetic studies the formation of $Co_4(CO)_8(PPh_3)_4$ was complete within a few minutes at room temperature Activation parameters were derived by least squares analysis of the dependence of $\log(k/T)$ on $1/T$. Reasonably good linear plots were obtained (Fig 3) but the scatter was somewhat greater than is usually observed in such studies, probably because of the pronounced sensitivity of the system to traces of O_2. The reactions under N_2 also probably suffer from the fact that without some decomposition there is insufficient CO present for the stoichiometric formation of $Co_2(CO)_6(PPh_3)_2$.

Discussion

The reaction products

Reaction of $Co_4(CO)_{12}$ with an excess of PPh_3 in n-heptane or dichloroethane at room temperature leads very rapidly to the known complex $Co_4(CO)_{11}(PPh_3)$ [1] but further reaction occurs observably slowly to form the previously unreported complex $Co_4(CO)_8(PPh_3)_4$. This formulation is supported by the analysis and by the spectroscopic titration that shows that 4 times as much PPh_3 is needed to form the product than is needed to form the $Co_4(CO)_{11}(PPh_3)$. The IR spectrum of $Co_4(CO)_8(PPh_3)_4$ shows the same major bands in heptane, DCE, and in Nujol and the spectrum is independent of whether the complex was isolated from heptane or DCE. General trends in the IR spectra (particularly the highest energy medium to strong bands) of $Ir_4(CO)_{12-n}L_n$ [7,8] and $Co_4(CO)_{12-n}L_n$ [3,4] also support this formulation as opposed, for instance, to $Co_4(CO)_9(PPh_3)_3$ For example $Co_4(CO)_9(PPhMe_2)_3$ has its highest energy band at 2037 cm^{-1} [3] and the corresponding band for $Co_4(CO)_9(PPh_3)_3$ would be expected at a higher energy. However, the highest energy medium to strong band of the new compound is at 2005 cm^{-1} which is consistent with a more highly substituted complex. The spectrum of $Co_4(CO)_8(PPh_3)_4$ is also very similar to that of the product isolated after reaction of $Co_4(CO)_{12}$ with dppm. This in turn can be assigned the formulation $Co_4(CO)_8(dppm)_2$ because of the very close similarity of its IR spectrum to that of $Rh_4(CO)_8(dppm)_2$ The analytical and spectroscopic data therefore provide good evidence that the product is $Co_4(CO)_8(PPh_3)_4$ rather than $Co_4(CO)_{10}(PPh_3)_2$, $Co_4(CO)_9(PPh_3)_3$, or $Co_2(CO)_6(PPh_3)_2$ Its spectrum is also quite different from that of $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$, which contains only a very weak band at 1955 cm^{-1} in DCE (together with strong bands at 2005 and 1885 cm^{-1}) but which also precipitates immediately from heptane on reaction of $Co_2(CO)_8$ with PPh_3 in contrast with the complete solubility of comparable amounts of $Co_4(CO)_8(PPh_3)_4$ in heptane at room temperature.

The main feature of the IR spectrum of $Co_4(CO)_8(PPh_3)_4$ that distinguishes it from other $Co_4(CO)_8L_4$ complexes [3] is the intense band at 1890 cm^{-1} and the weakness of the band at ca 1820 cm^{-1} The latter is conventionally assignable to bridging carbonyls which show values of $\nu(CO)$ from ca. 1860 cm^{-1} in $Co_4(CO)_{12}$ to 1792 cm^{-1} in $Co_4(CO)_8\{P(OMe)_3\}_4$ [3] The band at ca 1890 cm^{-1} is seen in $Co_4(CO)_{12}$, where it is very weak, and in $Co_4(CO)_{11}(PPh_3)$ [1]. In the latter complex it is weaker than the bridging bands at 1853 and 1835 cm^{-1} when the spectrum is measured in heptane but in DCE it is of equal intensity No band at 1890 cm^{-1} is shown by $Co_4(CO)_8\{P(OMe)_3\}_4$ in heptane but a weak shoulder is seen at ca 1910 cm^{-1} in DCE. Weak bands at 1890 cm^{-1} are also shown by $Co_4(CO)_8(dppm)_2$ in DCE and CS_2 The intensity of the band at 1890 cm^{-1} compared with that of the bridging carbonyls appears therefore to increase with increasing steric strain induced by substituents and it is also favoured by DCE as solvent compared with heptane We suggest that the bands at ca. 1890 cm^{-1} are due to semibridging carbonyls [9] and that the complexes probably exist in solution in different forms in equilibria, isomers with semibridging carbonyls becoming more preponderant as steric strain increases and when the solvent is changed from heptane to DCE The close similarity of the spectra in DCE and in suspension in Nujol suggests that the solid consists of the isomer with semibridging carbonyls Equilibria between isomers containing CO in various states of bridging have been proposed for $Fe_3(CO)_{12}$ and its substituted derivatives [10] and a very strong band at 1903 cm^{-1} has been assigned to semibridging carbonyls in $Fe_3(CO)_8(C_4H_8S)_2$ [11] Steric effects induce semibridging behaviour in $Cp_2Mo_2(CO)_4(C_2R_2)$ complexes to the extent that $\nu(CO)$ is reduced to as low as ca. 1840 cm^{-1} [9,12]. An investigation of the crystallographic structure of $Co_4(CO)_8(PPh_3)_4$ is clearly desirable and there seems to be no reason why crystals suitable for such a study should not be grown

The substitution kinetics

It is known that $Co_4(CO)_{11}\{P(OMe)_3\}$ reacts with $P(OMe)_3$ to form $Co_4(CO)_{10}\{P(OMe)_3\}_2$ at a rate essentially first order in $[P(OMe)_3]$ [4]. The rate constant observed by us for reaction of $Co_4(CO)_{11}(PPh_3)$ with PPh_3 in n-heptane is ca. 3×10^{-4} s^{-1} at ca. 20°C when $[PPh_3] = 6 \times 10^{-2}$ M so $k_2 \leq 5 \times 10^{-3}$ M^{-1} s^{-1}. As might be expected from steric considerations of the nature of the substituent already present [13], and of the entering ligand [14], this is substantially less than the value of 0.2 M^{-1} s^{-1} for k_2 at 20.6°C reported [4] for the bimolecular reaction of $Co_4(CO)_{11}\{P(OMe)_3\}$ with $P(OMe)_3$ The reaction of $Co_4(CO)_{11}(AsPh_3)$ with $AsPh_3$ is very much slower still, probably because of the weaker nucleophilic character of $AsPh_3$. Further reaction of $Co_4(CO)_{10}\{P(OMe)_3\}_2$ with $P(OMe)_3$ proceeds to form $Co_4(CO)_9\{P(OMe)_3\}_3$ and then $Co_4(CO)_8\{P(OMe)_3\}_4$.

A value of 1.4 × 10^{-3} s^{-1} is reported [4] for dissociative substitution of $P(OMe)_3$ into $Co_4(CO)_{10}\{P(OMe)_3\}_2$ at 48.4°C. Reaction of $Co_4(CO)_9\{P(OMe)_3\}_3$ with $P(OMe)_3$ is much slower and we obtained $k_{obsd} = 2 \times 10^{-4}$ s^{-1} at 60°C when $[P(OMe)_3] = 0.01$ *M*.

Although the reaction of $Co_4(CO)_{11}(PPh_3)$ with PPh_3 is slower than that of $Co_4(CO)_{11}\{P(OMe)_3\}$ with $P(OMe)_3$ it proceeds directly through to $Co_4(CO)_8(PPh_3)_4$ without there being any spectroscopic evidence for the intermediates $Co_4(CO)_{10}(PPh_3)_2$ or $Co_4(CO)_9(PPh_3)_3$; i.e. these intermediates are much more labile towards substitution than the corresponding complexes containing $P(OMe)_3$. $Co_4(CO)_{11}(PBu_3)$, on the other hand, reacts quite rapidly through to $Co_4(CO)_9(PBu_3)_3$ but further substitution is slow. Somewhat similar behaviour is found in reactions of $Ru_3(CO)_{12}$ with PPh_3 and $P(OMe)_3$ [14], and of $Ir_4(CO)_{12}$ with PPh_3, and considerably more work is required before the effects of various substituents and degrees of substitution on the reactivities of such clusters can be fully understood [4]. In this connection, the existence of $Co_4(CO)_8(PPh_3)_4$ appears to contrast unexpectedly with the absence of $Ir_4(CO)_8(PPh_3)_4$ and the latter may yet be shown to result from kinetic factors. Certainly no difficulty was experienced in preparing $Ir_4(CO)_8(PPh_2Me)_4$ or $Ir_4(CO)_8(PPh_2Et)_4$ [7].

Cluster fragmentation kinetics

The kinetics of fragmentation of $Co_4(CO)_8(PPh_3)_4$ in DCE to form $Co_2(CO)_6(PPh_3)_2$ show features similar to those of $Ru_3(CO)_9(PPh_3)_3$ [16]. Reaction under N_2 is independent of $[PPh_3]$ at $[PPh_3] \geq 0.05$ *M*, k_{obs} being 1.39 × 10^{-4} s^{-1}, with a mean deviation of 0.11 × 10^{-4} s^{-1}, from $[PPh_3] = 0.05$ to 0.15 *M*. However, when $[PPh_3]$ is decreased below 0.05 *M* the rate increases quite sharply, suggesting that a PPh_3-dissociative step can be rate determining. When the reaction is carried out under CO-N_2 mixtures the rate constants at $[PPh_3] = 0.05$ *M* decrease to a lower limiting value of 6 × 10^{-5} s^{-1} as *p*(CO), the partial pressure of CO, increases. This strongly suggests that ca. 50% of the reaction under N_2 at 60°C proceeds via rate-determining dissociation of CO. The third reaction path is independent of CO ($p(CO) \geqslant 40\%$) and of $[PPh_3]$ (0.03 to 0.12 *M*), k_{obs} being 5.8 × 10^{-5} s^{-1} with a mean deviation of 0.2 × 10^{-5} s^{-1} over these ranges. This path must therefore involve spontaneous activation of the cluster, i.e. activation without the need for preliminary dissociation of, or attack by, any ligands. Although the kinetics were followed in DCE in which the "semi-bridging" isomer (see above) appears to predominate, it is unlikely that solvent effects and the consequent differences in the detailed cluster structures would be very large. Energy differences between bridged, semi-bridged, and non-bridged isomers are likely to be quite small in view of rapid CO scrambling in such systems [3,17,18].

The very positive value of 27 cal K^{-1} mol^{-1} for $\Delta S^{\ddagger}$ is an indication that there is a high degree of Co—Co bond breaking or "loosening" of the Co_4 cluster on forming the transition state. In the corresponding spontaneous fragmentations of $Ru_3(CO)_{12-n}(PPh_3)_n$ ($n = 1$—3) [19] the values of $\Delta S^{\ddagger}$ increase from −23 to +7 cal K^{-1} mol^{-1} as *n* increases from 1—3. This was also rationalized in terms of an increased loosening, along the series, of the cluster bonding in the transition state caused essentially by the size of the PPh_3 substituents. Considerably greater loosening must occur in the $Co_4(CO)_8(PPh_3)_4$ cluster The values of $\Delta H^{\ddagger}$ for spontaneous fragmentation of $Co_4(CO)_8(PPh_3)_4$ and $Ru_3(CO)_9(PPh_3)_3$ [16] are almost the same and the lower kinetic stability of the Co_4 cluster is due to its more positive value of $\Delta S^{\ddagger}$ This implies that the bonding in the unexcited Co_4 cluster is weaker since a greater degree of loosening can be brought about by the same increase of enthalpy.

The value of $\Delta S^{\ddagger}$ for the path involving rate-determining CO dissociation is quite small (10 cal K^{-1} mol^{-1}) although smaller values are found for the corresponding CO-dissociative fragmentation reactions of $Ru_3(CO)_9L_3$ (L = PPh_3, $P(OPh)_3$, and P-n-Bu_3) [20] Small values of $\Delta S^{\ddagger}$ were ascribed to a tightening of the cluster bonding that offset the increased entropy of the dissociating CO

The stability towards fragmentation of $Co_4(CO)_8\{P(OMe)_3\}_4$ and $Co_4(CO)_8$-$(dppm)_2$ is considerably greater than that of $Co_4(CO)_8(PPh_3)_4$ $P(OMe)_3$ is about as good a σ-donor as PPh_3 [21] but is considerably smaller [22] and we therefore ascribe the greater ease of fragmentation of $Co_4(CO)_8(PPh_3)_4$ to a steric effect Steric effects clearly determine the ease of fragmentation of analogous Mn_2 complexes [23] The final reaction products of $Co_4(CO)_{12}$ with P-n-Bu_3, even after some hours at 80°C, do not appear to include any Co_2 products so it does not appear that the highly basic [21] and not particularly large [22] P-n-Bu_3 induces any instability in the Co_4 cluster. $Co_4(CO)_8(dppm)_2$ is also very resistant to fragmentation. The unsubstituted cluster $Co_4(CO)_{12}$ requires [24] one or two additional CO ligands in the transition state for it to undergo fragmentation to $Co_2(CO)_8$ at rates comparable to those of $Co_4(CO)_8(PPh_3)_4$ and the [CO]-independent rates of fragmentation of $Co_4(CO)_{12}$ are therefore much slower than those of the PPh_3-substituted complex Apart from the indication that steric effects may be an important factor, in the absence of more extensive quantitative data on the effects of substituents it is not possible yet to make any generalizations on the effects of substituents on the kinetic stability of the Co_4 cluster.

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