Reaction of bis(dimethylphosphino)ethane with the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$; synthesis, structure, and solution dynamics of $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$

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Abstract

The reaction of the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ (1) with the bidentate ligand 1,2-bis(dimethylphosphino)ethane (dmpe) gives the disubstituted cluster $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (3) in high yield. The dmpe ligand is bound to a single cobalt atom in a chelating fashion as determined by FT-IR and NMR (^{31}P and ^{13}C) spectroscopy and single-crystal X-ray crystallography. $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ $\cdot \frac{1}{2}$ toluene crystallizes in the triclinic space group $P\bar{1}$ with a 11.673(1), b 15.986(5), c 20.276(7) Å, α 94.40(3), β 106.28(2), γ 94.89(2)°, V 3599(2) Å^3 and $Z = 4$. Block-cascade least squares refinement yielded $R = 0.0521$ for 6830 reflections. The temperature-dependent ^{13}C NMR spectra of 3 reveal two distinct fluxional processes which serve to equilibrate the carbonyl ligands about the cluster polyhedron. The stability of 3 under different conditions has been examined by Cylindrical Internal Reflectance (CIR) spectroscopy. In benzene solution 3 is stable under 250 psi of H_2 at 150°C; partial decomposition to $Co(CO)_4^-$ is observed using CO and H_2/CO under analogous conditions.

Introduction

The reaction of metal clusters with polydentate phosphines has been extensively studied. Interest in this field derives from reports of enhanced cluster stability due

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to the presence of bridging and capping ligands [1], altered product distributions in catalytic reactions [2], and substrate activation via multielectron redox reactions [3]. To date, the majority of bridged polynuclear complexes have employed the aryl-substituted polyphosphines bis(diphenylphosphino)methane (dppm) [4,5], bis(diphenylphosphino)ethane (dppe) [6], and bis(diphenylphosphino)ethylene (dppt) [7,8]. However, such phosphine ligands, while useful, may serve to shield potentially reactive metal centers due to the spatially insulating effects transmitted by the aryl rings.

The use of alkyl-substituted polyphosphines has received much recent attention since the bridging of metal–metal bonds may be maintained while minimizing the unwanted steric bias associated with aryl-substituted polyphosphines. For example, the use of bis(dimethylphosphino)methane (dmpm) has been shown to afford bridged polynuclear complexes that display modified chemical reactivity relative to dppm-bridged compounds [9]. Increased aqueous solubility of dmpm derivatives relative to their aryl counterparts suggests that more active water-gas-shift catalysts are forthcoming [10].

In contrast to the plethoric examples of dmpm-bridged complexes, the corresponding bis(dimethylphosphino)ethane (dmpe) ligand has been little studied in its reaction with polynuclear systems. While many mononuclear dmpe complexes have been prepared and shown to possess a chelating dmpe ligand(s) [11], the ligand coordination mode in metal clusters remains to be established. Our interest in the reaction of dmpe with the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ stems from an earlier report of diphosphine bridging and chelation [12]. In this paper we describe the synthesis, spectral and crystallographic characterization of $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$. The stability of this new cluster complex is also described using Cylindrical Internal Reflectance (CIR) spectroscopy and the results are compared to that of the parent cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$.

Results and discussion

I. Synthesis

Treatment of the tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ (1) in either THF or benzene at room temperature with a stoichiometric amount of dmpe led to a rapid evolution of CO (2 mol) and the formation of the disubstituted cluster $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (3) as shown in Scheme 1. FT-IR analysis revealed the presence of 3 in greater than 95% yield which could be routinely isolated in 60–85% yield by chromatography using silica gel and benzene. A FT-IR spectrum of dark red 3 in CH_2Cl_2 is particularly informative as it suggests the presence of a chelating dmpe ligand (Fig. 1). The terminal carbonyl stretching bands of 3 (2038, 1999, and 1946 cm^{-1}) are observed at lower energy [13] relative to the parent cluster 1 consistent with disubstitution while the two bridging carbonyl bands at 1845 and 1812 cm^{-1} suggest an asymmetric environment for the μ_2-carbonyl groups [14]. The latter μ_2-carbonyl band is readily assigned to that group flanked by the chelating dmpe ligand [13]. Had the dmpe ligand adopted a bridging mode (i.e., ligation across a non-carbonyl-bridged Co–Co bond) the two μ_2-CO groups would have been rendered symmetrically equivalent. Such a ligation mode has been shown to afford a single μ_2-CO band in the IR spectrum of structurally analogous clusters [12]. The chelating nature of the dmpe ligand in 3 was also established by
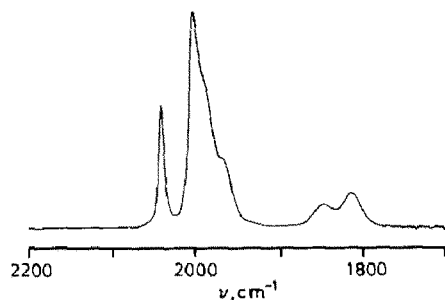
Fig. 1. Infrared spectrum of the carbonyl region for $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (3) in dichloromethane at room temperature.

variable-temperature ^{31}P and ^{13}C NMR measurements and X-ray crystallography (vide infra).

When the substitution reaction was monitored (in (THF) by FT-IR at $-15°C$ the intermediate mono-substituted cluster $Co_4(CO)_9(\mu_4\text{-PPh})_2(\eta^1\text{-dmpe})$ (2) was not observed; only the slow formation of 3 was observed under these conditions. Substitution reactions conducted at lower temperatures led only to 3 without the spectroscopic intermediacy of 2. Putative 2 with its dangling dimethylphosphine
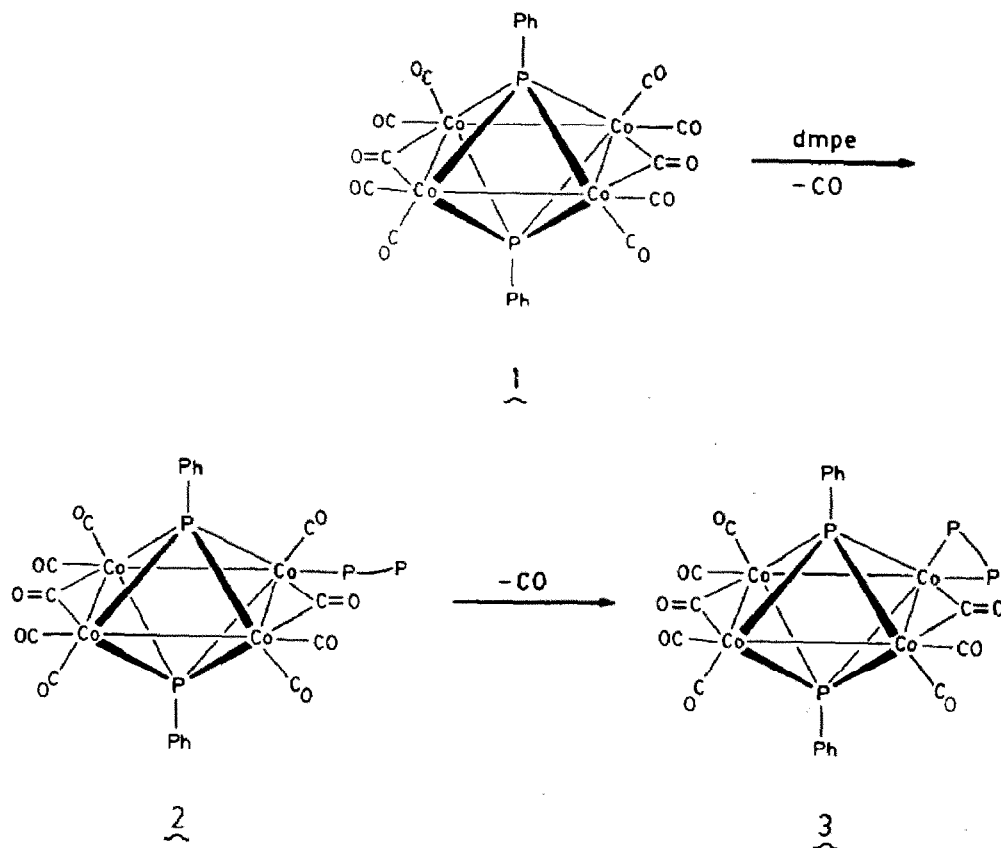
Scheme 1

group apparently undergoes a rapid chelate ring attack (Sn2-associative) [15] at the already substituted cobalt center to yield to observed disubstituted cluster **3** (Scheme I). Interestingly enough, a more favorable entropic contribution leads to chelate ring closure as opposed to bridge ring closure [16,17].

II. Molecular structure

The structure of **3** has been confirmed by single-crystal X-ray diffraction analysis. Crystals of **3** are observed to contain two fully independent molecules in the unit cell that are structurally similar in addition to one independent toluene solvent molecule. The cobalt clusters are loosely packed forming a cavity through the center of the cell and parallel to the c axis while the toluene molecules lie approximately in the plane and fill the packing voids. The X-ray data collection and processing parameters for **3** are given in Table 1 with the final fractional coordinates listed in Table 2.

The ORTEP diagram in Fig. 2 shows the molecular structure of **3** and unequivocally establishes the chelating nature of the dmpe ligand. Selected bond distances and angles are given in Tables 3 and 4, respectively. The four cobalt atoms are coplanar (rmsd 0.006 Å) and form a distorted rectangular array which is capped by a pair of μ_4-phenylphosphinidene groups giving an overall octahedral $Co_4(\mu_4\text{-P})_2$ core typical for this genre of cluster [18,19]. Each cobalt atom is seven-coordinate and the geometry is probably best described as a distorted capped octahedron. The central plane around each cobalt atom is composed of P(1), P(2) and either two terminal CO groups or P(3) and P(4) of the chelating dmpe ligand, e.g., in molecule A P(1)P(2)P(3)P(4) are coplanar (rmsd 0.04 Å) with Co(1) lying 0.293(1) Å out of the plane. Some of the chemically equivalent Co–Co bonds are not statistically equivalent in the two independent molecules which probably reflects an optimistic estimate of the standard deviations.

The four carbonyl-bridged Co–Co bond distances range from 2.509(1) to 2.524(1) Å with an average length of 2.518(6) Å. These bond lengths are comparable with the mean value of 2.520(2) Å observed in the similar carbonyl-bridged bonds in the parent cluster **1** [18]. The longer non-carbonyl-bridged Co–Co bonds are disparate in length and are responsible for the distorted rectangular array observed in **3**. The non-carbonyl-bridged Co–Co bond flanked by the dmpe ligand (Co(1)–Co(2)) is 2.797(9) Å (average) while the opposite bond length is 2.672(3) Å (average). The 0.125 Å difference between these bonds reflects the unfavorable steric interactions within the cluster polyhedron induced by the chelating dmpe ligand. Similar bond length perturbations in $Co_4(CO)_8(\mu_4\text{-PPh})_2(PPh_3)_2$ [20], $Co_4(CO)_7(\mu_4\text{-PPh})_2[P(OMe)_3]_3$ [21], and $Co_4(CO)_8(\mu_4\text{-PPh})_2(Ph_2PCH=CHPPh_2)$ [12] have been observed and attributed to the ancillary P-ligands.

The terminal Co–CO distances range from 1.770(7) to 1.798(8) Å with a mean distance of 1.779(8) Å. The four independent μ_2-CO groups do not bridge the cobalt atoms symmetrically as the bridging Co–CO distances vary from 1.834(6) to 2.060(6) Å. The μ_2-bridging Co–CO bond lengths adjacent to the dmpe ligand average 1.840(6) Å while the opposite Co(4)–C(8) bond lengths display a mean distance of 2.047(13) Å. This 0.207 Å difference may be ascribed to an electronic effect transmitted by the chelating dmpe ligand. Replacement of CO ligands with the better σ-donor dmpe ligand should lead to greater electron density on Co(1) [13], relative to the remaining cobalt atoms, manifesting itself in greater Co(1)–(μ_2)C
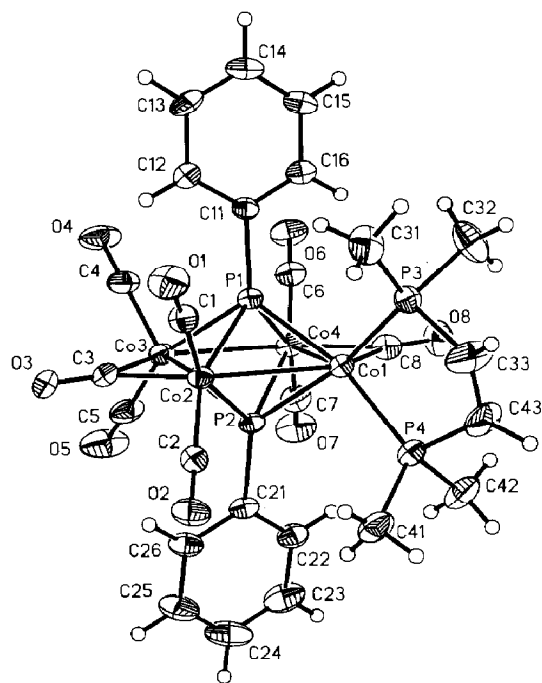
Fig. 2. ORTEP diagram of $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (3) with thermal ellipsoids drawn at the 30% probability level. The solvent molecule has been omitted for clarity.

Table 1

X-ray crystallographic collection and processing data for $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe) \cdot \frac{1}{2}$ toluene (3)

space group	$P\bar{1}$
cell constants	
a, Å	11.673(1)
b, Å	15.986(5)
c, Å	20.276(7)
α, deg	94.40(3)
β, deg	106.28(2)
γ, deg	94.89(2)
V, Å^3	3599(2)
mol formula	$C_{26}H_{24}Co_4P_4O_8 \cdot \frac{1}{2}C_7H_8$
fw	870.18
formula units per cell (Z)	4
ρ, g cm^{-3}	1.606
abs coeff (μ), cm^{-1}	20.29
radiatn (λ), Å	0.71073
collectn range, deg	$3.0° \le 2\theta \le 45.0°$
ω scan range (°)	2.0
total data collected	9396
independent data, $I > 3\sigma(I)$	6830
total variables	805
R	0.0521
R_w	0.0415
weights	$w = [\sigma^2(F_o) + 0.00090F_o^2]^{-1}$

Table 2

Positional parameters of non-hydrogen atoms for $Co_4(CO)_x(\mu_4\text{-}PPh)_2(dmpe)$ (3) with estimated standard deviations in parentheses.

	x	y	z	U^a		x	y	z	U^a
Molecule A									
Co(1A)	8108(1)	3045(1)	3236(1)	48(1)	C(4B)	6483(7)	7729(5)	2759(4)	68(3)
Co(2A)	10492(1)	3724(1)	3889(1)	50(1)	O(4B)	7121(5)	7245(4)	2960(3)	113(3)
Co(3A)	11155(1)	2474(1)	3327(1)	58(1)	C(5B)	6340(6)	8951(5)	1870(4)	68(3)
Co(4A)	8892(1)	1828(1)	2694(1)	57(1)	O(5B)	6886(5)	9249(4)	1554(3)	107(3)
C(1A)	10752(6)	3922(4)	4793(3)	66(3)	C(6B)	4142(7)	6399(5)	1648(4)	68(3)
O(1A)	10968(5)	4098(3)	5376(2)	103(3)	O(6B)	4452(6)	5751(3)	1749(3)	108(3)
C(2A)	10621(6)	4782(4)	3686(3)	57(3)	C(7B)	3845(6)	7446(4)	631(4)	65(3)
O(2A)	10689(5)	5468(3)	3580(3)	86(3)	O(7B)	3936(6)	7432(4)	82(3)	104(3)
C(3A)	12096(7)	3433(5)	3888(4)	70(3)	C(8B)	1892(6)	7214(4)	1247(3)	58(3)
O(3A)	13082(5)	3743(3)	4123(3)	91(3)	O(8B)	1213(4)	6708(3)	858(2)	89(2)
C(4A)	11816(7)	1631(5)	3752(4)	83(4)	P(1B)	3865(2)	7785(1)	2598(1)	46(1)
O(4A)	12224(6)	1057(4)	3998(4)	138(4)	C(11B)	4139(6)	7058(4)	3243(3)	55(3)
C(5A)	11815(8)	2471(5)	2634(4)	95(5)	C(12B)	4992(7)	7279(5)	3864(4)	77(4)
O(5A)	12253(7)	2449(5)	2205(4)	163(5)	C(13B)	5232(8)	6721(7)	4355(4)	101(5)
C(6A)	8805(7)	766(5)	2899(3)	70(3)	C(14B)	4640(10)	5922(7)	4233(5)	112(6)
O(6A)	8796(5)	73(3)	2986(3)	99(3)	C(15B)	3767(8)	5697(5)	3619(5)	88(5)
C(7A)	8740(7)	1626(4)	1792(4)	77(4)	C(16B)	3512(6)	6255(5)	3122(4)	66(3)
O(7A)	8709(6)	1453(4)	1233(3)	113(4)	P(2B)	3741(2)	8825(1)	1708(1)	46(1)
C(8A)	7219(7)	2111(4)	2679(4)	66(3)	C(21B)	3796(5)	9582(4)	1099(3)	47(3)
O(8A)	6265(5)	1760(3)	2425(3)	95(3)	C(22B)	3171(6)	9406(4)	399(3)	57(3)

P(1A)	9619(2)	2387(1)	3807(1)	47(1)			
C(11A)	9669(6)	1765(4)	4523(3)	52(3)			
C(12A)	10646(6)	1831(4)	5096(4)	64(3)			
C(13A)	10629(8)	1322(5)	5629(4)	78(4)			
C(14A)	9638(9)	762(5)	5566(4)	78(4)			
C(15A)	8689(8)	693(4)	5006(4)	73(4)			
C(16A)	8691(6)	1189(4)	4484(3)	63(3)			
P(2A)	9617(2)	3186(1)	2773(1)	49(1)			
C(21A)	9769(7)	3714(4)	2041(3)	56(3)			
C(22A)	8906(7)	3568(5)	1418(4)	76(4)			
C(23A)	9061(11)	3965(7)	869(4)	122(6)			
C(24A)	10069(13)	4509(7)	937(6)	143(8)			
C(25A)	10931(10)	4646(6)	1545(5)	109(5)			
C(26A)	10793(8)	4252(4)	2103(4)	74(4)			
C(31A)	7828(7)	3331(5)	4900(3)	106(4)			
C(32A)	5961(7)	2280(5)	3997(5)	120(5)			
P(3A)	7083(2)	3111(1)	4002(1)	63(1)			
C(33A)	6205(10)	3993(6)	3830(6)	150(7)			
C(43A)	5934(9)	4191(7)	3177(6)	151(7)			
P(4A)	7006(2)	3991(1)	2708(1)	68(1)			
C(41A)	7685(7)	5029(4)	2664(4)	98(4)			
C(42A)	6051(7)	3728(5)	1843(4)	113(4)			
C(3B)	5772(7)	9358(5)	3121(4)	67(3)			
O(3B)	6539(5)	9765(4)	3534(3)	98(3)			

C(23B)	3234(7)	9979(5)	-56(4)	80(4)
C(24B)	3933(8)	10738(5)	169(4)	95(4)
C(25B)	4557(8)	10923(5)	854(4)	88(4)
C(26B)	4494(6)	10349(4)	1315(3)	65(3)
C(31B)	1323(6)	7637(5)	3380(4)	85(4)
C(32B)	37(7)	6654(4)	2157(4)	94(4)
P(3B)	899(2)	7674(1)	2459(1)	65(1)
C(33B)	-249(8)	8401(6)	2325(6)	132(6)
C(43B)	-554(8)	8595(7)	1622(6)	165(7)
P(4B)	794(2)	8873(1)	1343(1)	80(1)
C(41B)	1012(8)	9992(5)	1456(5)	140(6)
C(42B)	169(7)	8673(6)	427(4)	137(5)
Toluene				
C(07)	7458	7100	-727	1393(47)
C(02)	7011(10)	5713(8)	-416(5)	382(18)
C(03)	6702	5299	101	659(32)
C(04)	6567	5764	679	237(12)
C(05)	6740	6644	741	244(12)
C(06)	7049	7059	224	298(16)
C(01)	7185	6593	-355	361(15)

ᵃ Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 3

Selected bond distances (Å) in the two independent molecules of $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (3)

	Molecule A	Molecule B		Molecule A	Molecule B
Co(1)–Co(2)	2.806(1)	2.788(1)	Co(4)–C(6)	1.781(8)	1.771(8)
Co(1)–Co(4)	2.524(1)	2.522(1)	Co(4)–C(7)	1.788(9)	1.772(9)
Co(2)–Co(3)	2.509(1)	2.515(1)	Co(4)–C(8)	2.034(9)	2.060(6)
Co(3)–Co(4)	2.669(1)	2.674(1)	C(1)–O(1)	1.145(8)	1.131(11)
Co(1)–P(1)	2.217(2)	2.208(2)	C(2)–O(2)	1.134(9)	1.138(10)
Co(1)–P(2)	2.219(2)	2.214(2)	C(3)–O(3)	1.165(9)	1.151(8)
Co(1)–P(3)	2.211(2)	2.205(2)	C(4)–O(4)	1.152(11)	1.139(10)
Co(1)–P(4)	2.212(2)	2.208(2)	C(5)–O(5)	1.126(14)	1.127(14)
Co(1)–C(8)	1.845(6)	1.834(6)	C(6)–O(6)	1.134(9)	1.139(10)
Co(2)–P(1)	2.261(2)	2.245(2)	C(7)–O(7)	1.136(11)	1.145(11)
Co(2)–P(2)	2.270(2)	2.272(2)	C(8)–O(8)	1.160(9)	1.161(7)
Co(2)–C(1)	1.770(7)	1.786(9)	P(1)–C(11)	1.812(7)	1.795(7)
Co(2)–C(2)	1.774(7)	1.777(8)	P(2)–C(21)	1.807(7)	1.805(6)
Co(2)–C(3)	1.968(9)	1.955(8)	P(3)–C(31)	1.777(7)	1.800(7)
Co(3)–P(1)	2.267(2)	2.273(2)	P(3)–C(32)	1.782(8)	1.807(7)
Co(3)–P(2)	2.279(2)	2.269(2)	P(3)–C(33)	1.811(11)	1.825(10)
Co(3)–C(3)	1.896(7)	1.930(7)	C(33)–C(43)	1.341(16)	1.435(17)
Co(3)–C(4)	1.771(8)	1.777(8)	P(4)–C(41)	1.797(7)	1.773(8)
Co(3)–C(5)	1.782(10)	1.798(8)	P(4)–C(42)	1.790(7)	1.787(7)
Co(4)–P(1)	2.258(2)	2.249(2)	P(4)–C(43)	1.807(13)	1.847(11)
Co(4)–P(2)	2.238(2)	2.254(2)			

backbonding and a shorter Co(1)–C(8) bond distance. The Co–(μ_4)P distances to the capping μ_4-phenylphosphinidene groups vary from 2.208(2) to 2.279(2) Å and display a mean length of 2.52(2) Å in agreement with other structurally characterized clusters of this class [12,18–22].

The phenyl rings attached to P(1) and P(2) in the two molecules are planar (rmsd 0.002 to 0.008 Å) and display a twist angle of 12(1)° (average). The P(1)··P(2) distances in the two molecules are 2.536(3) and 2.530(3) Å. When the chelate rings Co(1)P(3)C(33)C(43)P(4) are fitted to a least-squares plane, out-of-plane deviations are greater than 0.1 Å. Steric interactions between the methyl groups of the diphosphine and the phenyl groups of the μ_4-phenylphosphinidine tilt the phenyl rings away from the chelated diphosphine, e.g., H32A··H16A = 2.35(5), H43A··H22A = 2.22(5) Å. The shortest intermolecular contact is 2.24(5) Å between a toluene methyl hydrogen and a hydrogen atom attached to C(42).

III. Solution structure and dynamics

A $^{31}P\{^1H\}$ NMR spectrum of 3 in CDCl$_3$ at 298 K exhibits two, broad resonances at $\delta \sim 136$ and ~ 46 in a 1/1 integral ratio assignable to the pair of μ_4-phosphinidene caps and the chelated dmpe ligand, respectively [23]. When the solution was cooled to 223 K the ^{31}P resonances sharpened considerably as a result of thermal decoupling of the ^{59}Co ($I = 7/2$) nuclei from the ^{31}P nuclei [24]. Such a decoupling phenomenon has its origin in the increased molecular correlation time (τ_c) 3 experiences as the temperature is decreased. Longer τ_c's afford shorter spin-lattice relaxation times (t_1) for the cobalt nuclei which translate into diminished scalar coupling between the ^{31}P and ^{59}Co nuclei [25]. Elimination (or

diminution) of scalar $J(^{59}Co-^{31}P)$ values leads directly to sharper ^{31}P resonances and improved signal-to-noise in the low-temperature NMR spectrum. Finally, the ^{31}P chemical shifts were observed to be temperature invariant ruling out any fluxional processes involving the phosphinidene or dmpe ligands.

^{13}C NMR examination of **3** at 298 K revealed a single, broad resonance for the eight carbonyl groups at $\delta \sim 215$, indicating rapid intramolecular exchange of the carbonyl groups consistent with the reported dynamic behavior of similar phosphinidene-capped clusters [12,26,27]. To facilitate the variable-temperature NMR study necessary for elucidation of the exchange pathways available to the ancillary CO's a sample of **3** in benzene was treated with ^{13}CO (1 atm). Stirring for several days at temperatures up to 333 K resulted in minimal ^{13}CO enrichment in **3**. This observation suggests that dissociative CO loss in **3** is negligible and establishes the temperature-dependent ^{13}C NMR behavior as arising from intramolecular exchange processes (vide infra). ^{13}CO incorporation in **3** could be effected by near UV photolysis of **3** in benzene under ^{13}CO (1 atm). Typically, **3** was enriched to 20–30% (as determined by FT-IR) with cluster recovery routinely > 95% after photolysis.

Figure 3 shows the variable-temperature ^{13}C NMR spectra of **3**. The limiting spectrum was obtained at 183 K, revealing five carbonyl resonances at δ 247.5, 246.0, 208.0, 207.0, and 205.5 with a relative integral ratio of 1/1/2/2/2, respectively, completely consistent with the observed solid-state structure of **3**. The resonance at lowest field (δ 247.5) is readily assigned to the bridging carbonyl resonance adjacent to the dmpe-substituted cobalt center (i.e., Co(1)) with the δ 246.0 resonance representing the other bridging carbonyl group. The remaining terminal carbonyls may be confidently assigned based on their location relative to the dmpe ligand and their solution behavior. Here the δ 208.0, 207.0, and 205.5 resonances are assigned to (CO(6) + CO(7)), (CO(1) + CO(2)), and (CO(4) + CO(5)), respectively. The carbonyl groups closer to the dmpe ligand are expected to appear further downfield relative to the latter distal CO groups [12,28]. As the temperature is raised to 218 K the bridging carbonyl resonance of δ 246.0 broadens appreciably along with the two terminal carbonyl resonances at δ 207.0 and 205.5. Further warming to 228 K leads to near coalescence of these same resonances ($\tau_c \cong 233$ K) and suggests that rapid terminal ↔ bridge carbonyl exchange is occurring between these five carbonyl groups furthest from the dmpe ligand. The carbonyl groups

$\Delta G^{\ddagger} = 9.4$ kcal/mol

$\Delta G^{\ddagger} = 13.7$ kcal/mol
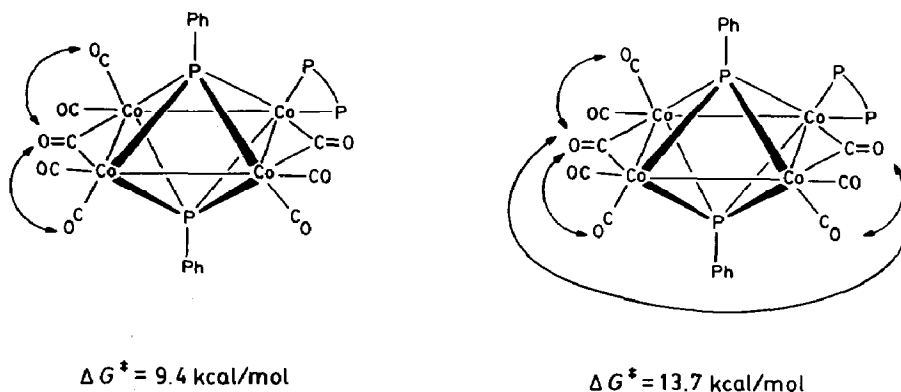
Scheme 2

Table **4**

Selected angles (°) in the two independent molecules of $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (**3**)

	Molecule A	Molecule B
Co(2)–Co(1)–Co(4)	88.7(1)	89.1(1)
Co(2)–Co(1)–C(8)	141.3(3)	142.7(2)
Co(4)–Co(1)–C(8)	52.8(3)	53.6(2)
Co(2)–Co(1)–P(1)	51.9(1)	51.8(1)
Co(4)–Co(1)–P(1)	56.5(1)	56.3(1)
C(8)–Co(1)–P(1)	97.0(2)	97.9(2)
Co(2)–Co(1)–P(2)	52.1(1)	52.5(1)
Co(4)–Co(1)–P(2)	55.9(1)	56.4(1)
C(8)–Co(1)–P(2)	99.3(3)	100.3(2)
P(1)–Co(1)–P(2)	69.7(1)	69.8(1)
Co(2)–Co(1)–P(3)	108.6(1)	107.5(1)
Co(4)–Co(1)–P(3)	132.1(1)	133.0(1)
C(8)–Co(1)–P(3)	97.8(3)	98.2(2)
P(1)–Co(1)–P(3)	99.5(1)	100.0(1)
P(2)–Co(1)–P(3)	160.8(1)	159.9(1)
Co(2)–Co(1)–P(4)	112.2(1)	109.5(1)
Co(4)–Co(1)–P(4)	127.8(1)	128.5(1)
C(8)–Co(1)–P(4)	96.4(2)	97.9(2)
P(1)–Co(1)–P(4)	164.0(1)	161.1(1)
P(2)–Co(1)–P(4)	99.4(1)	97.3(1)
P(3)–Co(1)–P(4)	87.3(1)	87.8(1)
Co(1)–Co(2)–Co(3)	88.2(1)	88.3(1)
Co(1)–Co(2)–C(1)	111.0(2)	110.4(2)
Co(3)–Co(2)–C(1)	123.4(2)	125.2(3)
Co(1)–Co(2)–C(2)	106.6(2)	110.7(2)
Co(3)–Co(2)–C(2)	126.6(2)	124.5(3)
C(3)–Co(3)–P(1)	98.8(3)	95.4(3)
C(4)–Co(3)–P(1)	93.2(3)	94.4(3)
C(5)–Co(3)–P(1)	155.3(3)	156.5(2)
Co(2)–Co(3)–P(2)	56.3(1)	56.4(1)
Co(4)–Co(3)–P(2)	53.1(1)	53.5(1)
C(3)–Co(3)–P(2)	95.6(2)	97.5(2)
C(4)–Co(3)–P(2)	155.8(3)	154.0(2)
C(5)–Co(3)–P(2)	93.2(3)	92.1(2)
P(1)–Co(3)–P(2)	67.8(1)	67.7(1)
Co(1)–Co(4)–Co(3)	91.0(1)	90.7(1)
Co(1)–Co(4)–C(6)	126.2(3)	125.0(3)
Co(3)–Co(4)–C(6)	105.1(2)	104.2(2)
Co(1)–Co(4)–C(7)	125.0(2)	123.2(2)
Co(3)–Co(4)–C(7)	107.9(3)	111.0(2)
C(6)–Co(4)–C(7)	98.6(3)	100.3(3)
Co(1)–Co(4)–C(8)	46.2(2)	45.8(2)
Co(3)–Co(4)–C(8)	137.1(2)	136.5(2)
C(6)–Co(4)–C(8)	100.4(3)	101.3(3)
C(7)–Co(4)–C(8)	101.6(3)	98.2(3)
Co(1)–Co(4)–P(1)	54.9(1)	54.8(1)
Co(3)–Co(4)–P(1)	54.0(1)	54.2(1)
C(6)–Co(4)–P(1)	94.4(2)	92.5(2)
C(7)–Co(4)–P(1)	160.3(3)	162.9(2)
C(8)–Co(4)–P(1)	90.5(2)	90.3(2)
Co(1)–Co(4)–P(2)	55.2(1)	54.9(1)
Co(3)–Co(4)–P(2)	54.5(1)	54.0(1)
C(6)–Co(4)–P(2)	158.5(2)	156.6(2)

Table 4 (continued)

	Molecule A	Molecule B
C(7)–Co(4)–P(2)	94.9(2)	96.3(2)
C(1)–Co(2)–C(2)	99.0(3)	97.1(4)
Co(1)–Co(2)–C(3)	136.4(2)	137.5(2)
Co(3)–Co(2)–C(3)	48.3(2)	49.2(2)
C(1)–Co(2)–C(3)	98.5(3)	96.3(3)
C(2)–Co(2)–C(3)	99.3(3)	97.5(3)
Co(1)–Co(2)–P(1)	50.5(1)	50.7(1)
Co(3)–Co(2)–P(1)	56.5(1)	56.7(1)
C(1)–Co(2)–P(1)	95.2(2)	95.8(2)
C(2)–Co(2)–P(1)	156.6(2)	160.4(2)
C(3)–Co(2)–P(1)	96.9(2)	95.6(2)
Co(1)–Co(2)–P(2)	50.5(1)	50.6(1)
Co(3)–Co(2)–P(2)	56.7(1)	56.3(1)
C(1)–Co(2)–P(2)	160.3(2)	160.2(2)
C(2)–Co(2)–P(2)	93.9(2)	95.9(2)
C(3)–Co(2)–P(2)	94.0(2)	96.7(2)
P(1)–Co(2)–P(2)	68.1(1)	68.1(1)
Co(2)–Co(3)–Co(4)	92.1(1)	91.9(1)
Co(2)–Co(3)–C(3)	50.8(3)	50.1(2)
Co(4)–Co(3)–C(3)	142.7(3)	141.9(3)
Co(2)–Co(3)–C(4)	125.9(3)	129.3(3)
Co(4)–Co(3)–C(4)	103.9(2)	100.9(2)
C(3)–Co(3)–C(4)	102.2(3)	103.0(3)
Co(2)–Co(3)–C(5)	126.7(3)	123.4(3)
Co(4)–Co(3)–C(5)	102.5(3)	105.4(2)
C(3)–Co(3)–C(5)	98.7(4)	99.1(3)
C(4)–Co(3)–C(5)	100.0(4)	100.1(4)
Co(2)–Co(3)–P(1)	56.2(1)	55.6(1)
Co(4)–Co(3)–P(1)	53.7(1)	53.3(1)
C(8)–Co(4)–P(2)	93.2(2)	92.4(2)
P(1)–Co(4)–P(2)	68.7(1)	68.4(1)
Co(2)–C(1)–O(1)	175.5(6)	176.9(7)
Co(2)–C(2)–O(2)	177.1(7)	175.2(8)
Co(2)–C(3)–Co(3)	81.0(3)	80.7(2)
Co(2)–C(3)–O(3)	136.4(6)	137.9(7)
Co(3)–C(3)–O(3)	142.6(7)	141.3(7)
Co(3)–C(4)–O(4)	176.6(7)	175.8(7)
Co(3)–C(5)–O(5)	177.8(8)	178.7(7)
Co(4)–C(6)–O(6)	174.0(8)	177.0(7)
Co(4)–C(7)–O(7)	174.6(7)	177.3(7)
Co(1)–C(8)–Co(4)	81.0(3)	80.5(2)
Co(1)–C(8)–O(8)	145.9(7)	149.1(6)
Co(4)–C(8)–O(8)	133.1(6)	130.4(6)
Co(1)–P(1)–Co(2)	77.6(1)	77.5(1)
Co(1)–P(1)–Co(3)	111.5(1)	111.3(1)
Co(2)–P(1)–Co(3)	67.3(1)	67.7(1)
Co(1)–P(1)–Co(4)	68.7(1)	68.9(1)
Co(2)–P(1)–Co(4)	111.2(1)	112.2(1)
Co(3)–P(1)–Co(4)	72.3(1)	72.5(1)
Co(1)–P(2)–Co(2)	77.4(1)	76.8(1)
Co(1)–P(2)–Co(3)	110.9(1)	111.2(1)
Co(2)–P(2)–Co(3)	67.0(1)	67.3(1)
Co(1)–P(2)–Co(4)	69.0(1)	68.7(1)
Co(2)–P(2)–Co(4)	111.6(1)	111.0(1)

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Table 4 (continued)

	Molecule A	Molecule B
Co(3)–P(2)–Co(4)	72.4(1)	72.5(1)
C(31)–P(3)–C(32)	101.4(4)	101.3(4)
Co(1)–P(3)–C(33)	106.7(4)	106.3(4)
C(31)–P(3)–C(33)	102.3(4)	102.7(5)
C(32)–P(3)–C(33)	101.6(4)	103.2(4)
P(3)–C(33)–C(43)	115.3(9)	109.3(8)
C(33)–C(43)–P(4)	116.8(8)	112.0(6)
Co(1)–P(4)–C(43)	106.8(4)	106.0(4)
C(43)–P(4)–C(41)	103.4(4)	104.6(5)
C(43)–P(4)–C(42)	101.9(4)	100.2(4)
C(41)–P(4)–C(42)	101.8(4)	101.3(5)

proximate to the dmpe are unaffected in this low-energy exchange process shown in Scheme 2. From the slow-exchange chemical shifts and the coalescence temperature T_c, we estimate this low-energy exchange process to have an activation energy of $\simeq 9.4$ kcal/mol [29] in agreement with the barrier for terminal $\leftrightarrow$ bridge exchange in other tetracobalt clusters of this genre [12,26]. Such facile terminal $\leftrightarrow$ bridge carbonyl exchange arises via a mutual exchange mechanism [30] similar to the one-for-one, two-center exchange mechanism reported by Lewis and co-workers for $Cp_2Rh_2(CO)_2L$ [where L = CO or $(PhO)_3P$] [31]. Futher warming serves to broaden the remaining resonances (Fig. 3d and 3e) as CO(6), CO(7) and CO(8) begin to exchange among themselves and with the other carbonyls on the opposite face of the cluster. By 318 K all eight carbonyls are completely equilibrated about the cluster polyhedron giving rise to a single, broad resonance of $\delta \sim 215$ (vide supra) in agreement with the weighted-average chemical shift of all the carbonyl resonances. The activation energy for this high-energy exchanges process is estimated at $\simeq 13.7$ kcal/mol [29].

IV. Solution stability studies using cylindrical internal reflectance spectroscopy

The tetracobalt cluster **1** and the bis-phosphine cluster $Co_4(CO)_8(\mu_4$-$PPh)_2(PPh_3)_2$ have been reported to function as catalysts in the hydroformylation

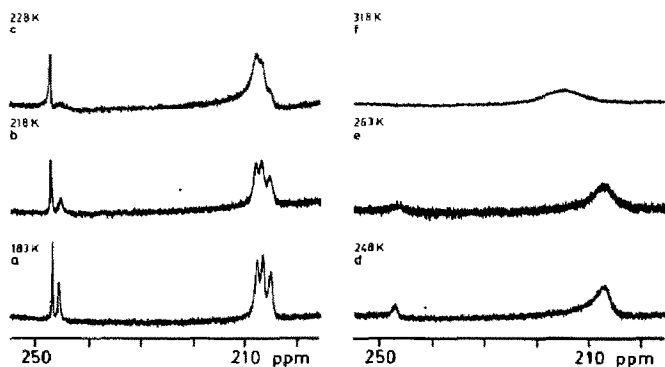Fig. 3. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of $Co_4(CO)_8(\mu_4$-PPh$)_2$(dmpe) (**3**) in 2-methyltetrahydrofuran/benzene-d_6.

of 1-pentene to aldehydes [20,32]. While the nature of the active catalyst remains obscure in each case, product selectivity studies and high yields of recovered cluster provide compelling evidence for catalysis arising from intact tetracobalt clusters. Accordingly, we felt that it was worthwhile to investigate the stability of **3** (in the absence of olefin) with CO, H_2/CO, and H_2 in order to probe the extent of cluster fragmentation or dmpe loss under model hydroformylation conditions. Our in situ stability studies described here were carried out in a high-pressure autoclave modified for solution measurements using Cylindrical Internal Reflectance (CIR) spectroscopy [33]. This method of spectral analysis offers many advantages over conventional high-pressure transmission IR cells as demonstrated by the elegant work of Moser and co-workers [34,35].

The CIR-FTIR reactivity studies were conducted in benzene using **3** ($\sim 2 \times 10^{-2}$ *M*) at an initial gas pressure of 250 psi. After recording the room temperature spectrum, the autoclave was heated up to and maintained at 150°C. Figure 4 shows the resulting CIR-FTIR spectra taken after 6 h. Reactions employing CO and H_2/CO (Fig. 4a and 4b) reveal partial decomposition of **3** based on the diminution of the starting carbonyl bands of **3** (compare with Fig. 1) and the growth of a broad band at ~ 1886 cm^{-1}. This new band is assigned to $Co(CO)_4^-$ which arises from a CO-induced disproportionation of **3** [36]. We have specifically not shown the counter cation for convenience's sake as it is most likely some form of Co^{2+} [37]. These reactions conducted under CO and H_2/CO lead to $\sim 75\%$ and $\sim 50\%$ fragmentation of **3**, respectively. **3** was the only material recovered (20 and 40%, respectively) after cooling, depressurization, and purification by chromatography.
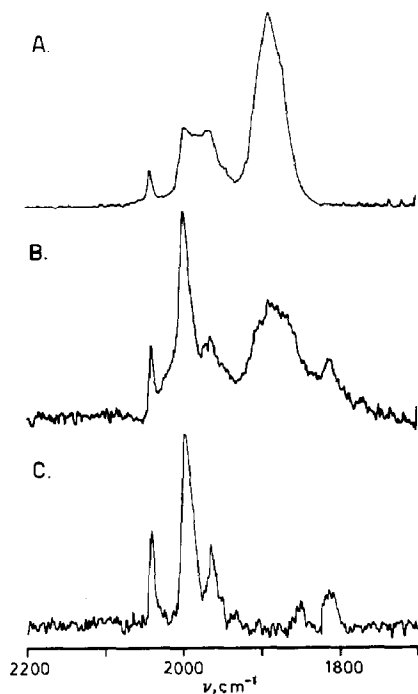

Fig. 4. CIR-FTIR spectra of $Co_4(CO)_8(\mu_4\text{-PPh})_2(dmpe)$ (**3**) at 150°C in the presence of A. CO, B. H_2/CO (1/1), and C. H_2. Initial loading pressure was 250 psi.

The fate of the dmpe ligand was not determined in these preliminary studies and no attempt was made to quantify the amount of $Co(CO)_4^-$ formed. Proof of a CO-induced cluster fragmentation manifold stems from the reaction of 3 with H_2. Figure 4c reveals only starting material after 6 h at 150°C. Furthermore, the observed stability of 3 is unexpected based on the facile fragmentation reactions involving other cobalt clusters under reducing conditions [38].

In the reactions with CO and H_2/CO it is noteworthy that at no time was the presence of 1 observed. This suggests that 3 does not lose its dmpe ligand to give $Co_4(CO)_{10}(\mu\text{-PPh})_2$ since the parent cluster displays greater stability than 3 under analogous conditions as determined by independent CIR-FTIR studies. For example, when 1 was heated at 150°C under 250 psi of CO for 6 h less than 15% decomposition to $Co(CO)_4^-$ was observed while the reaction under H_2/CO (1/1 ratio) gave $Co(CO)_4^-$ (~ 20%) along with the formation of a second species having a carbonyl band at ~ 2000 cm^{-1}. The reaction of 1 with H_2 reveals some conversion to this same species, but no $Co(CO)_4^-$ is observed. While the identity of this new species formed in the H_2/CO and H_2 reactions remains unknown, it is clear that $HCo(CO)_4$ and $Co_2(CO)_8$ are not present [39,40].

Finally, in comparison to $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$, 3 appears more susceptible towards fragmentation under CO and H_2/CO to give $Co(CO)_4^-$ as the only observable cobalt carbonyl by-product. This stability is reversed when clusters 1 and 3 are treated with H_2. This suggests that phosphine-substituted derivatives of 1 may yield novel hydrogenation catalysts based on polynuclear complexes rather than cluster fragmentation products. Catalytic hydrogenations and hydroformylations employing 3 are currently being examined and will be reported in due course along with CIR-FTIR spectral studies utilizing the parent cluster 1.

Experimental section

General

Dicobalt octacarbonyl and dichlorophenylphosphine were obtained from Pressure Chemical and used as received. Dmpe was purchased from Strem Chemical and used as received. $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ was prepared according to the procedure of Richmond and Kochi [41]. All reactions were conducted under argon using Schlenk techniques [42]. Benzene, toluene, THF, 2-methyltetrahydrofuran and heptane were distilled from sodium/benzophenone ketyl and stored under argon in Schlenk vessels. C_6D_6 was distilled from CaH_2 while $CDCl_3$ was distilled from P_2O_5 prior to use. $Cr(acac)_3$ was added as a shiftless relaxation agent in ~ 0.02 M concentration for the variable-temperature ^{13}C NMR study [43]. Carbon monoxide (99% ^{13}C enriched) was obtained from Isotec.

Infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer in 0.1 mm NaCl cells. Low-temperature IR spectra were recorded using a Specac Model P/N 21.000 variable-temperature cell equipped with CaF_2 windows. CCl_4/dry ice was used as coolant and the reported cell temperatures, taken to be accurate to $\pm 2°C$, were determined with the aid of a copper-constantan thermocouple. The ^{31}P and ^{13}C NMR spectra were recorded on JEOL FX-90X and Varian 300-VXR spectrometers, respectively. The ^{31}P NMR chemical shifts are referred to external 85% H_3PO_4 with positive chemical shifts to low field of the external standard. The ^{13}C NMR chemical shifts are referred to the ^{13}C resonance of C_6D_6 (δ 128). A

complete description of the procedure used to calculate the activation energies for carbonyl scrambling is given by Richmond and Kochi [12,44]. Microanalysis was performed by Atlantic Microlab, Atlanta, GA.

Synthesis of $Co_4(CO)_8(\mu_4\text{-}PPh)_2(dmpe)$

To 0.5 g (0.68 mmol) of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ in 100 ml of benzene was added ~ 0.12 ml of dmpe. The reaction mixture was stirred overnight, after which TLC examination (benzene) revealed essentially complete conversion to slower moving 3. The product was isolated by chromatography on silica gel using benzene. An analytical sample and crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a 1/1 mixture of toluene and heptane at $-25°C$: yield 0.47 g (83.3% yield based on 3) of dark red $Co_4(CO)_8(\mu_4\text{-}PPh)_2(dmpe)$; IR (CH_2Cl_2) $\nu(CO)$ 2038(s), 1999(vs), 1946(sh), 1845(w), 1812(w) cm^{-1}; $^{31}P\{^1H\}$ NMR $(CDCl_3)$ δ 136 (2P,s), 46 (2P,s). Anal. Found: C, 39.84; H, 3.65. $C_{26}H_{24}Co_4O_8P_4 \cdot \frac{1}{2}$ toluene calcd.: C, 40.59; H, 3.21%.

X-ray crystallography

A large, red crystal of dimensions $0.50 \times 0.60 \times 0.45$ mm was mounted on a Nicolet R3M/μ update of a P2$_1$ diffractometer. Cell constants were obtained from a least-squares refinement of 15 reflections in the range $18.08° \le 2\theta \le 25.32°$. Laue symmetry $\bar{1}$, no systematic absences and statistics are consistent with space group $P\bar{1}$. Intensity data in the range $3.0° \le 2\theta \le 45.0°$ were collected at 293 K in the ω Scan Mode using a variable scan speed and graphite-monochromated Mo-K_α radiation (λ 0.71073 Å). Two standard reflections were monitored periodically during data collection and no statistically significant changes were observed. Lorentz and polarization corrections and a ψ-scan based empirical absorption correction were aplied (transmission factors 0.261 to 0.362). The structure was solved by direct methods and refined by a block-cascade least-squares technique. All hydrogen atoms were located in a difference map but were allowed to ride at a fixed distance from the attached carbon atoms with a single fixed isotropic temperature factor. All other atoms were refined anisotropically. Refinement converged at $R = 0.0521$ and $R_w = 0.0412$ for 805 parameters and 6830 reflections.

CIR experiments

To a 15 ml CIR autoclave reactor (Barnes Analytical/Spectra Tech, Inc.) in a Vacuum/Atmospheres Dri-Lab (DXL series) was added ~ 0.15 g (0.18 mmol) of 3 and 8.0 ml of benzene. After sealing and removal from the Dri-Lab, the autoclave was pressurized with 250 psi with the desired gas(es). At this point the autoclave was transferred to an external sampling bench configured to the Nicolet 20SXB FT-IR spectrometer. The room temperature CIR-FTIR was recorded, after which the autoclave was heated to and maintained at $150°C$ for 6 h. The spectra shown in Fig. 4 were obtained from 250 signal-averaged spectra after solvent substraction. The CIR-FTIR spectra reported here were obtained using a TGS detector and a CIR autoclave reactor equipped with silicon optics.

Supplementary material available

Listings of observed and calculated structure factor amplitudes and tables of anisotropic thermal parameters, and idealized hydrogen parameters, ordering information will be supplied by the authors upon request.

Acknowledgments

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