does the desired "CpCo" transfer occur producing the new dinuclear complex $(\eta^5\text{-}C_5H_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ in addition to 1 but also the homodinuclear iridium analogue of composition $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Ir(\eta^5\text{-}C_5H_5)$. Attempts to run this reaction on a preparative scale have, however, been thwarted by the extreme reactivity of compounds of type $(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)_2M'(\eta^5\text{-}C_5H_5)$ (M/M′ = Co/Co, Co/Ir, Ir/Ir).[9b,31] Work in this and related areas is ongoing and will be reported in the near future.

Summary and Conclusions

A high-yield synthesis for the title complex $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2[Co(\eta^5\text{-}C_5H_5)]_2$ (**3**) is described and a detailed discussion of its properties in solution and in the solid state presented. The solid-state structure of **3** is derived from the unsaturated heterodinuclear precursor complex $(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)_2Co(\eta^5\text{-}C_5H_5)$ (**1**), to which a $Co(\eta^5\text{-}C_5H_5)$ fragment has been added. This observation fits neatly into the growing number of examples illustrating the isolobal concepts developed by Hoffmann and coworkers.[17] The unique CoCp fragment interacts strongly with the metal atoms of the dinuclear fragment and weakly with the two edge-bridging carbonyl ligands in the solid state. In solution, a low-energy CO scrambling process equilibrates the two CoCp fragments. **3** is paramagnetic in solution and in the solid state.

Trinuclear **3** is extremely labile by virtue of its formal 46 valence electron count and the reactivity of one of the CoCp fragments. Loss of this fragment is easily initiated by briefly exposing the complex to oxygen, ethylene, or mononuclear cyclopentadienyl dicarbonyl complexes. In all such cases the heterodinuclear precursor complex **1** is also produced initially. **3** readily adds carbon monoxide and catalyzes the decomposition of diazoalkanes to give saturated 48 valence electron cluster complexes, the latter case having a new μ-methylene group on the trinuclear frame. Thus **3** would appear to be a valuable synthetic precursor for a number of studies. On the one hand, small organic fragments are quite easily incorporated into **3** without disruption of the cluster backbone. Under other circumstances **3** appears to cleanly transfer a CoCp fragment to a variety of interesting substrates. These and other studies of the reactivity of **3** and similar analogues are in progress and will be reported in the near future.

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Registry No. **1**, 89371-07-3; **2**, 69393-67-5; **3**, 92957-47-6; **4**, 92957-48-7; **5**, 92957-49-8; $(\eta^5\text{-}C_5Me_5)Ir(CO)(\pi\text{-}C_2H_4)$, 92957-50-1; $CpCo(CO)(C_2H_4)$, 77674-12-5; $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, 32660-96-1; $CpIr(CO)_2$, 12192-96-0.

Supplementary Material Available: Table of observed and calculated structure factors and complete table (26 pages). Ordering information is given on any current masthead page.

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[31] Reaction of $CpIr(CO)_2$ with $CpCo(C_2H_4)_2$ has, under all conditions investigated thus far, yielded only a complex mixture of tri- and tetranuclear clusters.

Synthesis and Reactions of Thermally Stable Platinum(II) Carboxylic Acids (Hydroxycarbonyls) Containing Bis(tertiary phosphines)[†]

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Platinum(II) carboxylic acids (or hydroxycarbonyls) of general formula $Pt(CO_2H)(C_6H_9)(P\text{-}P)$ (C_6H_9 = 1-cyclohexenyl; P-P = $Ph_2PCH_2CH_2PPh_2$ (**1**), *cis*-$Ph_2PCH{=}CHPPh_2$ (**2**), $Ph_2PCH_2CH_2CH_2PPh_2$ (**3**), and $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (**4**)) have been prepared by the successive reaction of water and carbon monoxide with the cyclohexyne complexes $Pt(C_6H_8)(P\text{-}P)$. Complex **3** readily inserts a second molecule of CO into the platinum(II)–cyclohexenyl bond to give an acylplatinum(II) carboxylic acid, $Pt(CO_2H)(COC_6H_9)(Ph_2PCH_2CH_2CH_2PPh_2)$ (**5**). The complexes, which have been characterized by elemental analysis, IR spectroscopy and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, are monomeric in dichloromethane but appear to be associated through hydrogen bonds in the solid state. Complexes **1**–**5** do not decarboxylate in the solid state up to ca. 80 °C and do not form carboxylate ions by loss of a proton. These properties probably arise from the presence of nondissociating, strongly electron-donating ligands in the coordination sphere. The platinum(II) carboxylic acids do readily undergo esterification with alcohols, and **3** reacts with dimethylamine or *tert*-butylamine to give carbamoyl complexes $Pt(CONR^1R^2)(C_6H_9)(Ph_2PCH_2CH_2CH_2PPh_2)$ ($R^1 = R^2$ = Me, **6**; R^1 = *t*-Bu, R^2 = H, **7**). These reactions, and the ready exchange of ^{13}CO with the $Pt\text{–}CO_2H$ group, indicate that the carboxylic acids behave as $[Pt(C_6H_9)(CO)(P\text{-}P)]OH$, although the carbonyl cations could not be detected in solutions of the acids. Treatment of **5** with HBF_4 gives $[Pt(COC_6H_9)(CO)(Ph_2PCH_2CH_2CH_2PPh_2)]BF_4$, as expected, whereas **3** undergoes competitive cleavage of the platinum(II)–cyclohexenyl bond and consequent β-elimination of CO_2 from the $Pt\text{–}CO_2H$ group.

Introduction

Metallocarboxylic acids (hydroxycarbonyl metal complexes), L_nMCO_2H, have been proposed as key intermediates in several important reactions involving carbon monoxide. They include oxidation of CO (either free or coordinated) by metal ions,[1] the isotopic exchange of metal carbonyls with ^{18}O-labeled water (first observed by Muetterties),[2] the homogeneously catalyzed water gas shift

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[†] Dedicated to Professor Earl Muetterties, whose untimely death has deprived the inorganic and organometallic chemistry community of one of its most original and perceptive contributors.

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Table I. Carbon-13 NMR Data for Platinum(II) Carboxylic Acids $Pt(CO_2H)(C_6H_9)(P—P)$ and Derived Carbamoyl Complexes[a,b]

complex	solv	$\delta_{CO_2H/CONR_2}$	$^1J_{PtC}$	$^2J_{CP^1}$	$^2J_{CP^2}$
1	CD_2Cl_2	196.2	1320	157.3	8.5
2	CD_2Cl_2	195.0	1330	160.7	8.6
	$(CD_3)_2SO$	198.6	1291	159.0	8.6
3	CD_2Cl_2	196.4	1297	153.3	11.0
	$(CD_3)_2SO$	197.9	1274	152.2	10.3
4	CD_2Cl_2	194.7	1299	155.6	12.0
	$(CD_3)_2SO$	196.5	1270	153.9	12.0
5[c]	CD_2Cl_2	193.1	1265	132.5	12.2
6	$CDCl_3$	199.3	1185	140.0	11.0
	CD_2Cl_2	198.4	1176	141.0	ca. 11
7	CD_2Cl_2	195.5	1116	138.0	ca. 10

[a] Recorded on samples enriched to 90% with ^{13}C, chemical shifts being in parts per million to high frequency of Me_4Si; coupling constants in hertz. [b] Phosphorus atoms are labeled as in eq 1, 3, and 4 (see text). [c] $\delta_{COC_6H_9}$ 244.7, $^1J_{PtC}$ = 895 Hz, $^2J_{CP^1}$ = 8.7 Hz, and $^2J_{CP^2}$ = 105 Hz.

reaction,[3] and the reaction of metal carbonyls with base to give metal hydrides.[3,4] However, relatively few metallocarboxylic acids have been isolated and characterized and little is known about their chemistry. Fairly stable compounds of this class include $IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$,[5] $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$,[6] $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(NO)$,[7] $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(N_2Ar)$,[8] and $(\eta\text{-}C_5H_5)Mo(CO_2H)(CO)_2(PPh_3)$.[9] A communication from this laboratory which appeared in 1973[10] reported briefly the preparation of the first platinum(II) carboxylic acids $Pt(CO_2H)R(dppe)$ (R = CH_3, C_6H_9; C_6H_9 = 1-cyclohexenyl) by reaction of CO with the corresponding hydroxo complexes and noted their remarkable thermal stability, both in the solid state and in solution. Subsequently, analogous compounds $Pt(CO_2H)R(vdpp)$ (R = CH_2CN, CF_3; vdpp = *cis*-$Ph_2PCH{=}CHPPh_2$) have been reported,[11] and *trans*-$PtCl(CO_2H)(PEt_3)_2$ has been isolated from the reaction of *trans*-$[PtCl(CO)(PEt_3)_2]^+$ with water.[12] We report here in detail our work on platinum(II) carboxylic acids of the type $Pt(CO_2H)R(P\text{-}P)$ that contain bis(tertiary phosphines).[13] We have concentrated on complexes containing the 1-cyclohexenyl group (R = C_6H_9) because they are generally more stable and more soluble in organic solvents than the corresponding methyl compounds.

Experimental Section

Starting Materials. The following were obtained from the commercial suppliers given in parentheses: CO (Matheson), CO enriched to 90% in ^{13}C (Isotope Labeling Corp., Whippany, NJ), 40% aqueous HBF_4 (Ajax Chemicals), $HBF_4{\cdot}Et_2O$ (Aldrich), dimethylamine (Tokyo Kasei), *tert*-butylamine (EGA Chemie), and the bis(tertiary phosphines) dppe, vdpp, and dppp (Strem). 1,4-Bis(diphenylphosphino)butane (dppb)[14] and the cyclohexyne complex $Pt(C_6H_8)(dppe)$[15] were prepared by literature methods. The other cyclohexyne complexes $Pt(C_6H_8)(P\text{-}P)$ were prepared similarly to $Pt(C_6H_8)(dppe)$.[16]

Table II. Carbon-13 NMR Data for $Pt(CO_2H)(C_6H_9)(dppp)$ (3) in Various Solvents[a]

solv	δ_{CO_2H}	$^1J_{PtC}$	$^2J_{CP^1}$	$^2J_{CP^2}$
C_6D_6	196.0	1306	155.3	11.0
C_7D_8	195.5	1311	154.0	11.2
$CDCl_3$	196.9	1309	153.9	11.7
CD_2Cl_2	196.4	1297	153.3	11.0
THF-d_8	196.4	1298	155.0	12.0
$(CD_3)_2SO$	197.9	1274	152.2	10.3

[a] Coupling constants in hertz.

Spectroscopic Measurements. The following instruments were used for NMR measurements with an internal deuterium lock: JEOL FX 200 and Bruker CXP 200 (^1H and ^{13}C at 50.10- and 50.29 MHz, respectively) and Bruker CXP 200 (^{31}P at 80.98 MHz). Routine IR spectra were measured on a Perkin-Elmer 683 instrument. High-resolution IR spectra on dichloromethane solutions were recorded on a Perkin-Elmer 225 spectrometer with use of 0.1 mm matched, sealed KBr cells. The spectra were calibrated against the spectra of ammonia in the range 3491.4–3393.9 cm^{-1} and of water vapor in the range 1706.3–1417.5 cm^{-1}. NMR spectroscopic data for complexes **1**–**7** are in Tables I–III, and IR data for the carboxylic acids **1**–**5** are in Table IV.

Analyses were performed in the microanalytical laboratories of this school (Miss Brenda Stevenson and associates).

Preparations. (1) (1,3-Bis(diphenylphosphino)propane)(1-cyclohexenyl)(hydroxycarbonyl)platinum(II), $Pt(CO_2H)(C_6H_9)(dppp)$ (3). A solution of the cyclohexyne complex $Pt(C_6H_8)(dppp)$ (200 mg, 0.290 mmol) in THF (20 mL) was treated with water (10 mL). The clear, colorless solution was stirred at room temperature, the course of reaction being monitored by observing the disappearance of the $\nu(C{\equiv}C)$ band at ca. 1705 cm^{-1}; this usually required ca. 20 h. The solution was then evaporated to dryness under reduced pressure to give a white solid, $Pt(OH)(C_6H_9)(dppp)$. This was redissolved in THF (2 mL), and the straw-yellow solution was transferred into a test tube that was fitted with a septum cap secured by insulation tape and that contained a stirring bar. The solution was stirred under a pressure of carbon monoxide slightly above atmospheric for 10 min at room temperature. After the gas had been vented, the solution was treated with *n*-hexane to give a colorless solid. This was filtered off, washed with hexane, and dried in vacuo to give 190 mg (0.243 mmol, 84%) of **3**, mp 112–115 °C dec.

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(13) Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; vdpp = *cis*-vinylene-1,2-bis(diphenylphosphine), *cis*-$Ph_2PCH{=}CHPPh_2$; dppp = 1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2CH_2CH_2PPh_2$; dppb = 1,4-bis(diphenylphosphino)butane, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$.

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Table III. Phosphorus-31 and Proton NMR Data for Platinum(II) Carboxylic Acids $Pt(CO_2H)(C_6H_9)(P—P)$ and Derived Carbamoyl Complexes[a,b]

	δ_{P^1} ($^1J_{PtP^1}$)	δ_{P^2} ($^1J_{PtP^2}$)	$^2J_{PP}$	$\delta_{=CH\,of\,C_6H_9}$ ($^3J_{PtH}$, $^4J_{PH}$)	δ_{CO_2H}
1	39.7 (1897)	41.0 (1645)		5.25 (76, 9)	9.79
2	nm	nm		5.14 (75, 9)	9.82
3	−1.2 (1874)[c]	−6.0 (1610)[d]	22.6	5.05 (62, 7)	9.33
4	16.8 (1950)	6.6 (1666)	15.6	5.08 (76. 7)	9.26
5	−3.3 (1967)	−8.1 (1495)	26.3	ca. 7.15	9.37
6	−0.2 (1698)[e]	−7.2 (1610)[f]	ca. 20	4.90 (75, 8)[g,h]	
7	−1.2 (1519)[i]	−5.4 (1700)[j]	ca. 19	4.78 (73, 7)[e,k]	

[a] δ(P) in ppm relative to external 85% H_3PO_4 (positive to high frequency) and coupling constants in hertz, measured in CD_2Cl_2; ^{1}H NMR spectra measured in $(CD_3)_2SO$, except where indicated; P^1 trans to CO_2H or $CONR_2$ and P^2 trans to C_6H_9 or C_6H_9CO. [b] All complexes showed complex multiplets in the range δ 1–3 due to the CH_2 protons of the C_6H_9 group and of the bis(tertiary phosphines) and in the range δ 7–8 due to the aromatic protons. [c] $^2J_{CP^1}$ = 153 Hz. [d] $^2J_{CP^2} \simeq$ 11 Hz. [e] $^2J_{CP^1}$ = 140 Hz. [f] $^2J_{CP^2}$ = 11 Hz. [g] Measured in $CDCl_3$. [h] δ 2.28 (s, NMe), 2.59 (1:4:1t, NMe, $^4J_{PtH}$ = 5.3 Hz). [i] $^2J_{CP^1}$ = 138 Hz. [j] $^2J_{CP^2}$ = 9.6 Hz. [k] δ 5.31 (s, NH), 0.93 (s, *t*-Bu).

Table IV. IR Data (cm^{-1}) for $Pt(CO_2H)(C_6H_9)(P—P)$[a,b]

complex	labeling of COOH	ν(OH)	ν(C=O)	ν(C—O)
1	^{12}COOH	2670 w br	1630 w br	1215 m, 1160 m
	^{13}COOH	2660 w br	1610 m br	1185 m, 1160 m
2	^{12}COOH	2670 w br (3441 w)	1651 m, 1597 m (1652 s)	*c*
	^{13}COOH	2660 w br	1610 m, 1555 m	*c*
3	^{12}COOH	2680 w (3441 w)	1645 msh, 1605 s, (1648 s)	1153 m
		2650 w br (3435 w)	1600 msh, 1565 s (1615 s)	1127 m
	^{12}CO^{18}OH	2670 w br (3428 w)	1635 msh, 1600 s (1647 m, 1632 m)	*c*
4	^{12}COOH	2680 w (3431 w)	1645 msh, 1595 s	1145 m
			(1652 s)	*c*
	^{13}COOH	2660 w br	1610 msh, 1560 s	1120 m
5	^{12}COOH	2690 w (3436 w)	1640 msh, 1610 s[d] (1656 s)[e]	1153 m, 1137 m (1156 m)
	^{13}COOH	2665 w br	1625 msh, 1571 s[f]	1135 m, 1115 m

[a] Measured in KBr disks; values in parentheses refer to CH_2Cl_2 solution. [b] Abbreviations: br, broad; m, medium; s, strong; sh, shoulder; w, weak. [c] Band due to ν(C—O) could not be located unequivocally owing to overlap with bands due to the bis(tertiary phosphine), either in KBr disk or in CH_2Cl_2 solution. [d] ν(C=O) for $^{12}COC_6H_9$: 1563 s cm^{-1} (KBr). [e] ν(C=O) for $^{12}COC_6H_9$ 1565 cm^{-1} (CH_2Cl_2). [f] ν(C=O) for $^{13}COC_6H_9$: 1532 s cm^{-1} (KBr).

Anal. Calcd for $C_{34}H_{36}O_2P_2Pt{\cdot}0.7THF$: C, 56.33; H, 5.33; P, 7.92; mol wt, 734. Found: C, 56.47; H, 5.26; P. 7.95; mol wt by osmometry, 761 (CH_2Cl_2), 735 (pyridine).

The complexes $Pt(CO_2H)(C_6H_9)(P\text{-}P)$ (P-P = dppe (1), vdpp (2), and dppb (4)) were prepared similarly from the appropriate cyclohexyne complexes in yields of 40%, 27%, and 84% respectively. In the case of 1 and 2, the carbonylated solution contained insoluble, unidentified solid. This was removed by centrifugation, and the supernatant liquid was then decanted and treated with hexane.

Anal. Calcd for $C_{33}H_{32}O_2P_2Pt{\cdot}0.5THF$ (2): C, 55.78; H, 4.81; P, 8.22. Found: C, 55.80; H, 4.77; P, 8.40. Calcd for $C_{35}H_{38}O_2P_2Pt{\cdot}0.1THF$ (4): C, 56.32; H, 5.18; P, 8.21; mol wt, 748. Found: C, 56.01; H, 5.21; P. 7.76; mol wt (CH_2Cl_2), 864.

1 was characterized on the basis of its IR and ^{13}C NMR spectra. In all cases, the presence of THF of crystallization was confirmed by ^{1}H NMR spectroscopy; the proportions given are those that best fit the analytical data. The ^{13}C-labeled analogues of 1–4 were prepared similarly from 90% enriched ^{13}CO.

(2) (1,3-Bis(diphenylphosphino)propane)(cyclohexenecarbonyl)(hydroxycarbonyl)platinum(II), $Pt(CO_2H)(COC_6H_9)$(dppp) (5). A sample of $Pt(OH)(C_6H_9)$(dppp) was prepared as described above from $Pt(C_6H_8)$(dppp) (75 mg, 0.109 mmol) in THF (8 mL) and water (4 mL). The solid was dissolved in benzene (1 mL), and the solution was syringed into a tube under ca. 100 kPa of CO. The pressure was increased to 1200 kPa, and the solution was stirred at room temperature for 5 h. The voluminous white solid was removed by centrifugation, washed with hexane, and dried in vacuo to give 55 mg (0.072 mmol, 66%) of 5.

Anal. Calcd for $C_{35}H_{36}O_3P_2Pt$: C, 55.19; H, 4.76; P, 8.13; mol wt, 762. Found: C, 54.89; H, 4.85; P, 7.71; mol wt (CH_2Cl_2) 728.

If a pressure of 50–100 kPa is used, the reaction requires ca. 24 h at room temperature for completion.

(3) (1,3-Bis(diphenylphosphino)propane)(1-cyclohexenyl)(dimethylcarbamoyl)platinum(II), $Pt(CONMe_2)(C_6H_9)$(dppp) (6). A stirred solution of 3 (60 mg, 0.078 mmol) in THF (1 mL) was treated with gaseous dimethylamine (10 mL, ca. 0.45 mmol) from a syringe, and the mixture was allowed to stand at room temperature for 24 h. Addition of hexane precipitated a creamy solid that was recrystallized from THF/hexane to give colorless crystals of 6 (50 mg, 0.063 mmol, 81%). The labeled analogue $Pt(^{13}CONMe_2)(C_6H_9)$(dppp) was prepared similarly from 90% ^{13}C-enriched 3. Carbon analyses for 6 were inexplicably irreproducible: IR (KBr) 1583 (C=O) cm^{-1}.

Anal. Calcd for $C_{36}H_{41}NOP_2Pt$: C, 56.84; H, 5.43; N, 1.84. Found: C, 58.22, 55.69; H, 5.54, 5.37; N, 1.67, 1.75.

(4) (1,3-Bis(diphenylphosphino)propane)(1-cyclohexenyl)(*tert*-butylcarbamoyl)platinum(II), Pt(CONH-*t*-Bu)(C_6H_9)(dppp) (7). This was prepared similarly to 6 from 3 (60 mg, 78 mmol) and *tert*-butylamine (52 mg, 64 mmol). After the product had been recrystallized from THF/hexane, the yield of 7 was 52 mg (64 mmol, 82%): IR (KBr) 3420, 1566 (NH), 1538 (C=O) cm^{-1}.

Anal. Calcd for $C_{38}H_{45}NOP_2Pt$: C, 57.86; H, 5.75; N, 1.78. Found: C, 57.46; H, 5.76; N, 1.50.

Reaction of 3 with Alcohols. (1) NMR Experiments. An approximately 0.023 M solution of 3 (0.6 mL) in the appropriate deuterated solvent (see text) was allowed to react in an NMR tube with 0.55 μL of dry methanol (ca. 0.14 mmol, 10% excess). The progress of the reaction was followed by monitoring the appearance of the $Pt\text{–}CO_2CH_3$ signal at δ 2.98.

(2) IR Experiments. In each case, 0.25 mL of ca. 0.16 M 3 in CH_2Cl_2 was mixed with a tenfold excess of the alcohol (ca. 0.4 mmol) and the solution was placed in a 0.1-mm path-length KBr cell. The progress of the reaction over a period of ca. 1 h was followed by monitoring the decay of the band at 1650 cm^{-1} due to 3 and the concomitant growth of the ester absorption at ca. 1625 cm^{-1}. The reaction with methanol was complete within 1 min, those with ethanol and benzyl alcohol required ca. 25 min, and that with 2-propanol was incomplete after 1 h. With the assumption that the extinction coefficients of the ν(C=O) bands

Table V. Carbon-13 and Phosphorus-31 NMR Data for $[Pt(COC_6H_9)(CO)(dppp)]BF_4$ (**8**)[a]

	δ_X	$^1J_{PtX}$, Hz	other coupling const (J, Hz)[b]
C^1	221.8	591	P^2C^1, 80
C^2	174.9	1446	P^1C^2, 115
P^1	−9.7	3413	P^1C^2, 115; P^1C^1, 4
P^2	−8.3	1420	P^2C^1, 80; P^2C^2, 9

[a] Measured in CD_2Cl_2; see text for atom numbering. [b] P^1P^2, 41 Hz.

in the acid and ester are equal, the extent of reaction with 2-propanol was estimated as 56% after 1 h.

There was no reaction between **3** and *tert*-butyl alcohol or triethylamine under the same conditions.

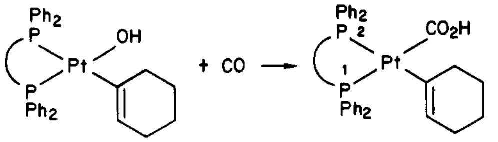
Reaction of 5 with Acid. A 0.046 M solution of 90% enriched $Pt(^{13}CO_2H)(^{13}COC_6H_9)(dppp)$ in dichloromethane (1.7 mL) was treated in an NMR tube with an equimolar quantity of $HBF_4{\cdot}Et_2O$ (9.7 μL, 0.078 mmol) dissolved in CD_2Cl_2 (0.1 mL). The sole product of the reaction was identified as $[Pt(COC_6H_9)(CO)(dppp)]BF_4$ on the basis of its ^{13}C and ^{31}P NMR spectra (Table V). Solvent was removed in vacuo to yield a yellow-brown solid: IR (KBr) 2056 s ($^{13}C{\equiv}O$), 1589 m, 1568 m ($^{13}C{=}O$) cm^{-1}, (CH_2Cl_2) 2060 s ($^{13}C{\equiv}O$), 1590 m, 1568 m ($^{13}C{=}O$) cm^{-1}.

Reaction of 3 with Acid. An ca. 0.16 M solution of **3** in dichloromethane (0.25 mL) was treated with an equimolar quantity of $HBF_4{\cdot}Et_2O$ (5 μL, ca. 0.04 mmol) or of 40% aqueous HBF_4 (6 μL). The solution was transferred to a 0.1-mm path-length KBr cell, and its IR spectrum was scanned periodically over a 24-h period. The characteristic bands of **3** were replaced immediately after the addition by bands at ca. 2330 and 2107 cm^{-1} assigned, respectively, to CO_2 and $[Pt(C_6H_9)(CO)(dppp)]^+$. The former grew at the expense of the latter with time. When the experiment was carried out on ^{13}C-labeled **3** in CD_2Cl_2, a peak due to $^{13}CO_2$ at δ 125.3 was observed in the ^{13}C NMR spectrum.

Reaction of 3 with CO. In a typical experiment, a 0.033 M solution of 90% enriched $Pt(^{13}CO_2H)(C_6H_9)(dppp)$ in dichloromethane (2 mL) was stirred under CO (50–100 kPa). Saples (ca. 0.2 mL) were withdrawn periodically and their IR spectra recorded in a 0.1-mm path-length KBr cell. Over a period of 3 h the $\nu(^{13}C{=}O)$ band of the starting material at 1565 cm^{-1} disappeared and was replaced by $\nu(^{12}C{=}O)$ bands at 1605 and 1563 cm^{-1} due to the CO_2H and COC_6H_9 groups, respectively, of $Pt(CO_2H)(COC_6H_9)(dppp)$ (**5**).

Results

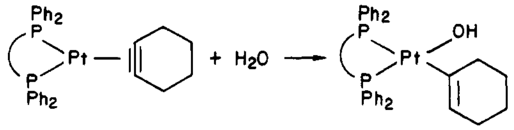
Preparation and Spectroscopic Characterization. Platinum(II) carboxylic acids of general formula $Pt(CO_2H)(C_6H_9)(P\text{-}P)$ have been prepared by insertion of carbon monoxide into the Pt–OH bond of the corresponding hydroxo complexes (eq 1). The latter are made



(1)

P P = dppe (**1**), vdpp (**2**), dppp (**3**), dppb (**4**)

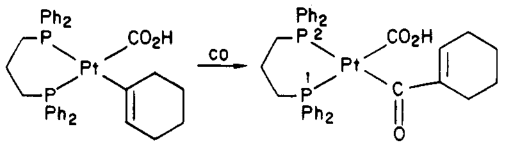
by protonation of the corresponding (cyclohexyne)platinum(0) complexes with water (eq 2)[15] and can be used directly in eq 1 without isolation or purification.



(2)

The reaction of CO with the hydroxoplatinum(II) complexes is complete within ca. 10 min at room temperature, but the yields of carboxylic acid depend strongly on the pressure of CO, on the bis(tertiary phosphine) present, on the solvent, and on the concentration of starting complex. In the case of the complexes of dppp and dppb, treatment of ca. 1.5 × 10^{-4} M solutions of the hydroxo complexes with CO at slightly above atmospheric pressure gives the corresponding carboxylic acids **3** and **4** quantitatively. Poorer yields are obtained if higher concentrations of the hydroxo complexes are allowed to react with CO at or below atmospheric pressure. Separate experiments show that there is a competing reaction between the starting hydroxo complexes and the product carboxylic acids that gives poorly soluble, as yet uncharacterized solids. In the case of the dppe and vdpp complexes, this competing reaction occurs even under ca. 10 atm of CO, although yields of **1** and **2** can be increased by using dichloromethane in place of THF and by reducing the concentration of the hydroxo complex to ca. 2.5 × 10^{-5} M.

A further complication is that the initially formed complex $Pt(CO_2H)(C_6H_9)(dppp)$ (**3**) reacts further with CO at room temperature to give, after several hours, a second platinum(II) carboxylic acid, $Pt(CO_2H)(COC_6H_9)(dppp)$ (**5**), containing an acyl group formed by insertion of CO into the Pt–C_6H_9 bond (eq 3). The corresponding methyl ester $Pt(CO_2Me)(C_6H_9)(dppp)$ reacts similarly with CO,[17] and studies in progress show that most 1-cyclohexenyl dppp complexes of the type $PtX(C_6H_9)(dppp)$ (X = various anionic ligands) behave in the same way. For complexes containing different bis(tertiary phosphines), the rate of insertion of CO into the Pt–C_6H_9 bond is in the order dppp > dppb ≫ dppe > vdpp. For this reason, under the conditions described in the Experimental Section, only the dppp system gives an acyl metallocarboxylic acid.



(3)

The platinum(II) carboxylic acids **1** and **2** are colorless, amorphous solids that are poorly soluble in water and most organic solvents. Complexes **3**–**5** are microcrystalline and insoluble in water but very soluble in CH_2Cl_2, $CHCl_3$, THF, and $(CH_3)_2SO$. Osmometric measurements on **3**, **4**, and **5** in dichloromethane, and on **3** in pyridine, show them to be monomeric in these solvents. The compounds have been characterized largely on the basis of NMR and IR spectroscopy. The ^{13}C NMR spectra of samples prepared by use of 90% enriched ^{13}CO exhibit a doublet of doublets at δ ca. 195, with ^{195}Pt satellites, due to the carboxylic carbon atom that is coupled to cis- and trans-phosphorus atoms [$^2J_{CP}$(trans) = 130–160 Hz; $^2J_{CP}$(cis) = 8–12 Hz] (Table I). The magnitude of $^1J_{PtC}$, ca. 1300 Hz, is similar to that reported for *trans*-$PtCl(CO_2H)(PEt_3)_2$ (1337 Hz)[12] and establishes that the carboxylic acid group is attached to platinum through carbon. The chemical shift of the carboxylic carbon atom varies very little for different bis(tertiary phosphines). It is ca. 20 ppm to higher frequency than that of *trans*-$PtCl(CO_2H)(PEt_3)_2$ and at slightly lower frequency than those of $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$ and $(\eta\text{-}C_5H_5)Mo(CO_2H)(CO)_2(PPh_3)$.[9] Both the chemical shift and the magnitude of $^1J_{PtC}$ show little dependence on solvent (Table II).

The $^{31}P\{^1H\}$ NMR spectra of the carboxylic acids, measured at 80.98 MHz, consist of a slightly distorted AX pattern with ^{195}Pt satellites (Table III). The variation of the chemical shifts of the phosphorus nuclei of the dppe (**1**), dppp (**3**), and dppb (**4**) complexes reflects the incor-

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[17] Bennett, M. A.; Rokicki, A. *J. Organomet. Chem.* **1983**, *244*, C31.

poration of these atoms into five-, six-, and seven-membered rings, respectively.[18] In the ^{31}P NMR spectrum of $Pt(^{13}CO_2H)(C_6H_9)(dppp)$, the resonances at δ -1.2 (J_{PtP} = 1874 Hz) and -6.0 (J_{PtP} = 1610 Hz) show couplings with ^{13}C of 153 and ca. 11 Hz, respectively, establishing that the first resonance is due to P^1 trans to CO_2H and the second signal is due to P^2 trans to C_6H_9. The resonances due to P^1 and P^2 for the remaining compounds have been assigned on the assumption that the relative magnitudes of $^1J_{PtP^1}$ and $^1J_{PtP^2}$ remain similar. These magnitudes reflect the high trans influence of the C_6H_9 and CO_2H ligands and confirm that the carboxylic acid group is C bonded to platinum. As expected,[19] the magnitude of $^1J_{PtP}$ trans to C_6H_9 (ca. 1600–1650 Hz) is less than that trans to the more electron-withdrawing carboxylic acid group (1870–1970 Hz).

The ^{13}C NMR spectrum of the cyclohexenecarbonyl carboxylic acid **5**, made by use of 90% enriched ^{13}CO, shows a doublet of doublets with ^{195}Pt satellites at δ 244.7 due to the acyl carbon atom, in addition to a similar pattern centered at δ 193.1 due to the carboxylic acid carbon. The chemical shift of the acyl carbon and the magnitudes of its associated coupling constants (Table V) are very similar to those reported for the chelate acyl complexes $[\overline{\mathrm{Pt(OC_6H_4C}}\mathrm{O)(PBu_3)_2}]^{+}$[20] and $\overline{\mathrm{PtL_2COCOCPh{=}C}}\mathrm{H}$ (L = various tertiary phosphines or $^1/_2$dppe)[21] and confirm that carbon monoxide has inserted into the Pt–C_6H_9 bond, not into the Pt–CO_2H bond. In the $^{31}P\{^1H\}$ NMR spectrum of **5**, the magnitude of $^1J_{PtP^2}$ trans to C_6H_9CO, 1495 Hz, indicates that the cyclohexenylcarbonyl group has an even higher trans influence than cyclohexenyl. This finding is in agreement with the conclusion drawn from the Pt–Cl distances in *trans*-$PtCl(CH_3)(PMePh_2)_2$[22] and *trans*-$PtCl(COCH_3)(PMePh_2)_2$[23] that acetyl has a higher trans influence than methyl.

The ^1H NMR spectra of the cyclohexenyl carboxylic acids **1**–**4** show no OH resonance in common NMR solvents such as $CDCl_3$, CD_2Cl_2, benzene-d_6, or toluene-d_8, either owing to self-exchange or because the signal is masked by the phenyl resonances of the bis(tertiary phosphines). However, in $(CD_3)_2SO$, a solvent that is known to suppress self-exchange of protons in organic compounds and also shifts OH resonances to high frequency, the OH resonances of **1**–**4** appear as a slightly broad singlet, without ^{195}Pt satellites, in the region δ 9–10; cf. $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(NO)$ δ 9.47 (CD_2Cl_2)[7c] and 8.6 (CD_3CN);[7a] $(\eta\text{-}C_5H_5)Re(N_2Ar)(CO_2H)(CO)$, δ 8.9 (solvent not specified);[8] $PtCl(CO_2H)(PEt_3)_2$, δ 11.0 (toluene-d_8), 8.5 (CD_3CN), and 8.6 (benzene-d_6).[12] The OH resonance of **5** can be observed in most common NMR solvents, the chemical shifts being δ 8.05 (CD_2Cl_2), 9.06 (benzene-d_6), and 9.37 ($(CD_3)_2SO$). It is not known whether the absence of ^{195}Pt satellites is due to the small magnitude of $^4J_{PtH}$, to self-exchange, or to exchange with traces of moisture. Exchange of water with the carboxylic acid proton was demonstrated by double-resonance experiments. Thus, irradiation of the resonance due to water in $(CD_3)_2SO$ solutions of **3** or **5**, or addition of D_2O to a solution of **3** in $(CD_3)_2SO$ or of **5** in benzene, caused the $PtCO_2$*H* signal to disappear.

The IR spectra of the platinum(II) carboxylic acids (Table IV) show a band due to ν(OH) at ca. 2680 cm^{-1} in KBr disks that shifts to ca. 3440 cm^{-1} in dichloromethane. The first value is within the range observed for hydrogen-bonded organic carboxylic acids (2700–2500 cm^{-1}), and the latter is only slightly below the range for monomeric carboxylic acids (3560–3500 cm^{-1}).[24] The IR spectrum of **3** in a mull of poly(chlorotrifluoroethylene), which is clear in the range of interest, showed the 2680 cm^{-1} absorption but there was no band in the 3400–3600 cm^{-1} region. In pyridine, the OH band of **3** appears at 2670 cm^{-1}, a value that is characteristic of a strongly hydrogen-bonded OH···N system.[25] These data suggest that the platinum(II) carboxylic acids are associated through hydrogen bonds in the solid state and confirm that they are monomeric in dichloromethane, a solvent of only moderate polarity. In contrast, organic carboxylic acids are associated through hydrogen bonds even in the gas phase.[24] Unfortunately, few data for other metallocarboxylic acids are available for comparison, viz., $PtCl(CO_2H)(PEt_3)_2$, 3140 cm^{-1} (solid),[12] $IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$, 3295 (solid) and 3313 cm^{-1} ($CHCl_3$),[5] $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$, 2700 cm^{-1} (solid),[6] and $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(NO)$, 2960 cm^{-1} (THF).[7c]

In a KBr disk, the ν(C=O) absorption of complexes **3**–**5** generally appears as a strong band with a shoulder of medium intensity on the high-frequency side in the region 1600–1650 cm^{-1}. In dichloromethane or pyridine, there is a single strong band at ca. 1650 cm^{-1}. The solid-state spectra of **1** and **2** show only one broad and ill-defined band at ca. 1650 cm^{-1}, perhaps because these complexes are amorphous rather than microcrystalline. A band or pair of bands in the region 1100–1200 cm^{-1} may be due to a coupled ν(C—O)/δ_{OH} mode of the CO_2H group. Similar ν(C=O) and ν(C—O)/δ_{OH} absorptions have been reported for other metallocarboxylic acids; the former are somewhat lower than those observed for organic carboxylic acids (1650–1740 cm^{-1}).

The frequency of the ν(C=O) band of $Pt(C^{18}OOH)(C_6H_9)(dppp)$[26] in a KBr disk is equal, within experimental error, to that of unlabeled **3**, although in solution the band in the labeled compound is split (Table IV). If the CO_2H proton had ionized reversibly, the ^{18}O label should have been distributed equally between the two possible sites and a band due to $\nu(C{=}^{18}O)$ at ca. 1610–1620 cm^{-1} should have been observed.[27] Thus the lack of such a band supports the chemical observations (see below) that the platinum(II) carboxylic acids have negligible acidic properties. The conclusion must be regarded as tentative because we could not locate the band due to $\nu(C\text{–}^{18}O)$ in $Pt(C^{18}OOH)(C_6H_9)(dppp)$; it may be masked by ligand absorptions.

Chemical Properties. In contrast to *trans*-$PtCl(CO_2H)(PEt_3)_2$, the platinum(II) carboxylic acids **1**–**5** show no tendency to decompose by elimination of CO_2, either in the solid state on exposure to air or in vacuo at tem-

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(24) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Chapman and Hall: London, 1975; p 183.

(25) Bellamy, L. J. "Advances in Infrared Group Frequencies"; Chapman and Hall: London, 1975; p 241.

(26) Prepared by treating $Pt(C_6H_8)(dppp)$ successively with $H_2{}^{18}O$ and CO.

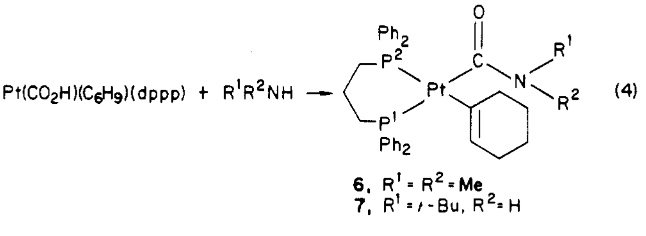
(27) The calculated isotope shift for a C=O bond behaving as a simple harmonic oscillator with a frequency of 1650 cm^{-1} is $1650 - 1650(20/21)^{1/2}$, i.e., 40 cm^{-1}. For ^{18}O-labeled benzophenone the ν(C=O) band is at 1635 cm^{-1}, compared with 1664 cm^{-1} in the unlabeled material (Halmann, M.; Pinchas, S. *J. Chem. Soc.* **1958**, 1703). The corresponding shifts in the ["ν(C=O)" bands at ca. 1570 cm^{-1} in metal acetylacetonates range from 12 to 26 cm^{-1} (Pinchas, S.; Silver, B. L.; Laulicht, I. *J. Chem. Phys.* **1967**, *46*, 1506. Musso, H.; Junge, H. *Tetrahedron Lett.* **1966**, *33*, 4003).

peratures up to 80 °C. They melt with decomposition above 100 °C, but the decomposition products have not yet been identified; preliminary studies show that a hydride is not formed. Solutions of the compounds in benzene, tetrahydrofuran, or dimethyl sulfoxide are stable in the absence of air, though a solution of **3** in dimethyl sulfoxide decomposes with loss of the CO_2H group at 90 °C. Solutions in dichloromethane or chloroform are stable for several hours but decompose on prolonged storage, probably by reaction with traces of HCl. The platinum(II) carboxylic acids fail the standard tests for organic carboxylic acids; e.g. they do not dissolve in 5% aqueous KOH, they neither dissolve in nor react with aqueous $KHCO_3$, and they are not deprotonated by triethylamine or 1,8-bis(dimethylamino)naphthalene. Complex **3** does react with 5 M aqueous KOH, *tert*-butyllithium, and triethylaluminum, but irreversible decomposition occurs and the products have not been identified. In contrast, treatment of *trans*-$[PtH(CO)(P\text{-}i\text{-}Pr_3)_2]BPh_4$ with an excess of KOH in aqueous THF has been reported to give the potassium salt of a platinum(II) carboxylic acid, *trans*-$PtH(CO_2K)(P\text{-}i\text{-}Pr_3)_2$.[28]

Despite their lack of acidity, the platinum(II) carboxylic acids readily form esters. When a solution of **5** in $CDCl_3$ is treated with a small excess of methanol, the CO_2H resonance at δ 8.06 rapidly disappears and is replaced by a singlet with ^{195}Pt satellites at δ 2.98 (J_{PtH} = 6.3 Hz) due to the methyl ester $Pt(CO_2CH_3)(COC_6H_9)(dppp)$. This compound has been made independently by treatment of the methoxo cyclohexenyl complex $Pt(OCH_3)(C_6H_9)(dppp)$ with an excess of CO.[17] Similarly, when a twofold excess of methanol is added to a solution of **3** in $(CD_3)_2SO$, the CO_2H resonance at δ 9.33 disappears over a period of a week and a new singlet due to $Pt(CO_2CH_3)(C_6H_9)(dppp)$ appears at δ 2.82. Esterification occurs much more rapidly in other solvents, e.g., within minutes at room temperature in $CDCl_3$ or CD_2Cl_2 and within hours in benzene-d_6. The progress of the reaction in dichloromethane can also be followed by observing the decrease in intensity of the ν(C=O) band of the acid at ca. 1650 cm^{-1} and the corresponding growth of the ester band at ca. 1625 cm^{-1}. Qualitatively, for different alcohols, the rate of esterification is $CH_3OH > C_2H_5OH \approx C_6H_5CH_2OH > (CH_3)_2CHOH$; *tert*-butyl alcohol does not form an ester.

When the methyl ester $Pt(CO_2CH_3)(C_6H_9)(dppp)$ is dissolved in wet $(CD_3)_2SO$, a weak signal at δ 9.33 due to the corresponding acid is observed after several hours at room temperature. This shows that esterification is reversible, although formation of the methyl, ethyl, and benzyl esters is strongly favored.

Complex **3** also reacts readily with dimethylamine and *tert*-butylamine at room temperature to give the corresponding acid amides **6** and **7** (eq 4). Their IR spectra show a ν(C=O) band at ca. 1580 cm^{-1} that is typical for carbamoyl complexes[29] and is ca. 100 cm^{-1} to lower frequency than those for organic acid amides.[30] In addition to the usual cyclohexenyl and dppp resonances, the ^1H NMR spectrum of the dimethylcarbamoyl complex **6** shows two distinct $N-CH_3$ singlets at δ 2.28 and 2.59 owing to restricted rotation about the C⎓N bond. The lower field signal shows ^{195}Pt satellites ($^4J_{PtH}$ = 5.3 Hz) and is assigned to the methyl group trans to platinum, following earlier work on platinum(II) carbamoyl complexes.[30] The ^{13}C NMR spectra of the carbamoyl complexes made from $Pt(^{13}CO_2H)(C_6H_9)(dppp)$ show a doublet of doublets with ^{195}Pt satellites at δ ca. 199 due to the carbamoyl carbon atom ($^1J_{PtC} \simeq$ 1200 Hz, $^2J_{CP}$(trans) $\simeq$ 140 Hz, $^2J_{CP}$(cis) $\simeq$ 11 Hz), the chemical shift being in the range 183–218 ppm recently reported for a range of organometallic carbamoyl complexes.[31] The $^{31}P\{^1H\}$ NMR spectra of the carbamoyl complexes, like those of the parent acids, consist of an AX pattern with ^{195}Pt satellites. As in the case of **3**, assignment of the ^{31}P chemical shifts has been based on the magnitude of $^2J_{CP}$ derived from the ^{31}P spectra of ^{13}C-enriched complexes. Surprisingly, the magnitude of $^1J_{PtP}$ trans to the carbamoyl ligands (1698 Hz in **6**; 1519 Hz in **7**) is lower than that trans either to CO_2H (1874 Hz) or to CO_2CH_3 (1882 Hz), which indicates that the carbamoyl ligands have a markedly higher trans influence than CO_2H or CO_2CH_3. In **7** the magnitude of $^1J_{PtP}$ trans to C_6H_9, 1700 Hz, is ca. 100 Hz larger than in **6** and in a series of complexes of the type $PtY(C_6H_9)(dppp)$.[16] The cause of these effects is not known, although steric repulsion between the mutually cis *tert*-butylcarbamoyl and cyclohexenyl substituents probably plays a role.



6, R¹ = R² = Me
7, R¹ = *t*-Bu, R² = H

The other platinum(II) carboxylic acids react with amines similarly to **3**, but in the case of **5** reaction occurs at both the carboxylic acid group and the acyl group, and the resulting mixture of products has not been identified.

The reactions of **1**–**5** with alcohols and amines to form esters and carbamoyl complexes, respectively, probably proceed by initial dissociation of OH^- to give a platinum(II) carbonyl cation (eq 5). This is supported by the order of

$$Pt(CO_2H)(C_6H_9)(P\text{-}P) \rightleftharpoons [Pt(C_6H_9)(CO)(P\text{-}P)]^+ + OH^- \quad (5)$$

reactivity of **3** with alcohols, which closely parallels that found in a kinetic study of the reaction of *trans*-$[PtCl(CO)(PPh_3)_2]^+$ with alcohols to form the esters *trans*-$PtCl(CO_2R)(PPh_3)_2$.[32] The acid $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$ ionizes completely in formamide (ϵ 109.5) to give $[(\eta\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+OH^-$, identified by its ν(C≡O) bands;[6] in contrast, the IR spectrum of a solution of **3** in *N*-methylformamide (ϵ ~200) shows no ν(C≡O) band in the region 2500–1800 cm^{-1}, so the carbonyl cation must be present in undetectably low concentration. Further evidence for the ionization described by eq 5 is that dichloromethane solutions of ^{13}CO-labeled **3** and **4** exchange completely with ^{12}CO in the carboxylic acid group over a period of 1 h at room temperature; in the case of **3** exchange is accompanied by insertion into the $Pt-C_6H_9$ bond to give **5**. Likewise, complex **5** exchanges with ^{13}CO only in the carboxylic acid group, the acyl C=O group being unaffected. The planar platinum(II) cations $[Pt(C_6H_9)(CO)(P\text{-}P)]^+$ could be expected to exchange rapidly with ^{13}CO by an S_N2 process; indeed $[PtCl_2(CO)]_2$ was reported many years ago to undergo "instantaneous" exchange with ^{14}CO.[33]

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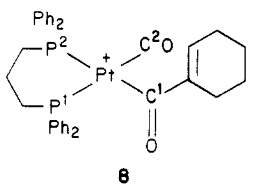
Characteristic of many of the metallocarboxylic acids reported in the literature is the reaction with protons to produce metal carbonyl cations (eq 6), which often is the

$$L_nM\text{-}CO_2H + H^+ \rightarrow L_nM^+\text{-}CO + H_2O \qquad (6)$$

reverse of the reaction used to prepare the acids. This reaction takes place quantitatively when **5** is treated with $HBF_4{\cdot}OEt_2$ in dichloromethane to give the (cyclohexenecarbonyl)platinum(II) carbonyl cation **8**, which has a terminal $\nu(^{13}CO)$ frequency of 2060 cm^{-1}. The complex has been identified unequivocally on the basis of its ^{13}C NMR spectrum, which shows resonances with the appropriate couplings for the acyl and terminal carbonyl carbon atoms (Table V). In the ^{31}P NMR spectrum, the Pt–P coupling constant for the phosphorus atom P^1 trans to terminal CO has the expected magnitude (3413 Hz), consistent with the low NMR trans influence of CO,[19] whereas J_{PtP^2} is very low (1420 Hz), confirming the very high trans influence of the cyclohexenecarbonyl ligand.



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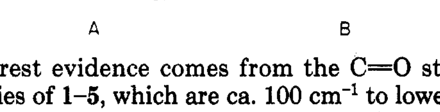
The reaction of the cyclohexenyl complex **3** with either $HBF_4{\cdot}OEt_2$ or 40% aqueous HBF_4 is more complex. The expected carbonyl cation $[Pt(C_6H_9)(CO)(dppp)]^+$ is formed, as shown by a $\nu(CO)$ band at 2107 cm^{-1} in the IR spectrum of the solution, but there is also a band at 2330 cm^{-1} assigned to free CO_2 that grows in intensity with time at the expense of the $\nu(CO)$ band. The presence of CO_2 was also confirmed by ^{13}C NMR spectroscopy, but the platinum-containing products could not be identified.

Discussion

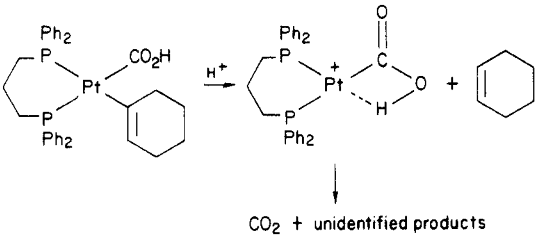
The preparation of complexes **1**–**5** by insertion of CO into a M–OH bond represents an alternative approach to the synthesis of metallocarboxylic acids, which have generally been made by nucleophilic attack of OH^- on a carbonyl group attached to a strongly electron-withdrawing metal center. The difference between the two methods is more apparent than real, however, because our reaction probably goes via a platinum(II) carbonyl intermediate. This could be a salt, $[Pt(CO)(C_6H_9)(P\text{-}P)]OH$, or a neutral five-coordinate complex, $Pt(OH)(C_6H_9)(CO)(P\text{-}P)$. These intermediates are also likely to be involved in the reactions of the carboxylic acids with alcohols and amines (eq 5).

The spectroscopic data for **1**–**5**, and for most other metallocarboxylic acids, suggest that there is strong electron donation from the metal to the hydroxycarbonyl group. This can be expressed in terms of a resonance contribution to the bonding from a dipolar form:



The clearest evidence comes from the C=O stretching frequencies of **1**–**5**, which are ca. 100 cm^{-1} to lower energy than those of typical organic carboxylic acids. It has been noted[29] that the C=O stretching frequencies of carbamoyl complexes are likewise ca. 80 cm^{-1} lower than those of typical carboxamides, an effect we also observe in the case of **6** and **7**, and a similar explanation has been advanced. The ^{13}C chemical shifts of the bound carboxylic carbon atoms in **1**–**5** are 10–20 ppm to higher frequency (lower field) than those of organic carboxylic acids (δ 165–185).[34] A contribution from the dipolar resonance form B will make the carboxylic carbon atom more carbene-like, and in fact the chemical shifts of **1**–**5** are in the lower part of the range reported for platinum(II)–carbene complexes.[35] The fact that these chemical shifts are also at higher frequency than that of *trans*-$PtCl(CO_2H)(PEt_3)_2$[12] could be because tertiary phosphines are better σ-donors than Cl^-, although this does not account for the similarity of the Pt–C coupling constants between **1**–**5** and *trans*-$PtCl(CO_2H)(PEt_3)_2$.

Scheme I. Decomposition of $Pt(CO_2H)(C_6H_9)(dppp)$ (**3**) by Acid



Complexes **1**–**5** resemble organic carboxylic acids in being associated through hydrogen bonds in the solid state but differ from them in being monomeric in solution, even in a relatively nonpolar solvent such as dichloromethane. This is probably a reflection of the fact that **1**–**5** show no tendency to form carboxylate ions and are, therefore, weaker acids $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(NO)$,[7c] $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$[6] and $(\eta\text{-}C_5H_4)Re(CO_2H)(CO)(NO)$,[7c] both of which are soluble in KOH. Presumably this lack of acidity is a consequence of the presence of strongly electron-donating ligands in **1**–**5**.

Complexes **1**–**5** differ from $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$ and $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(NO)$ in their thermal stability toward decarboxylation. For example, $(\eta\text{-}C_5H_5)Fe(CO_2H)(CO)(PPh_3)$ rapidly loses CO_2 on warming in benzene solution, whereas its potassium salt is stable to 100 °C in dry formamide.[6] On the other hand, $(\eta\text{-}C_5H_5)Re(CO_2H)(CO)(NO)$ does not lose CO_2 in anhydrous acetone at 50 °C; the anion $[(\eta\text{-}C_5H_5)Re(CO_2)(CO)(NO)]^-$ is readily decarboxylated on heating in dry solvents but is stabilized by water, presumably owing to hydrogen bonding.[7c] We suggest that **1**–**5** are stable to decarboxylation because the bidentate phosphines and the σ-bonded carbon ligand do not readily dissociate, so that it is not easy to create a vacancy in the coordination sphere that could accommodate CO_2, the product of β-elimination. Although a five-coordinate intermediate $PtH(C_6H_9)(CO_2)(P\text{-}P)$ might be thought to form readily, in practice this pathway seems to be energetically unfavorable. Evidence for this is the fact that the first step in the thermal decomposition of bis(alkyl) bis(tertiary phosphine) complexes $PtR_2(PR'_3)_2$ is dissociation of tertiary phosphine.[36] The first step in the facile thermal decarboxylation of *trans*-$PtCl(CO_2H)(PEt_3)_2$[12] may well be dissociation of Cl^- rather than of PEt_3, since we have found that the phenyl derivative *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ is stable in benzene or dichloromethane at room temperature.[16]

The necessity for a vacant coordination site to allow β-elimination to occur also accounts for the formation of

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CO_2 when complex 3 is treated with acid. In this case, the vacant site is generated by protonation of the platinum(II)-cyclohexenyl bond and elimination of cyclohexene (Scheme I). Evidently the platinum(II)-acyl bond in 5 is not so readily cleaved by acid, so that β-elimination of CO_2 from the CO_2H group cannot occur and the alternative reaction, viz., removal of OH^- from the CO_2H group, takes over.

As a general conclusion, metallocarboxylic acids seem to be structurally analogous to organic carboxylic acids, but their chemistry is dominated by their abnormal dissociation to $[L_nMCO]^+OH^-$. Their acid-base behavior and the tendency of the CO_2H group to lose CO_2 depend sensitively on the nature of the metal and of the associated ligands in a way that will only be revealed by further studies on related systems.

Substitutional Reactivity of Dodecacarbonyltrimetal Complexes of Iron and Osmium[†]

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The kinetics of the substitution reactions of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been investigated for L = PPh_3, PBu_3, $P(OPh)_3$, and $P(OMe)_3$ in hydrocarbon solution. The substitution of the iron cluster leads to both substitution and fragmentation products with a very small dependence on the entering ligand, typical of a CO dissociative interchange mechanism. Substitution of $Fe_3(CO)_{11}PPh_3$ leads only to fragmentation at a rate which is faster than substitution on $Fe_3(CO)_{12}$. Substitution on $Os_3(CO)_{12}$ occurs in an entering ligand independent reaction to $Os_3(CO)_9L_3$. The reactivities of these clusters are compared to the ruthenium analogue and to the mononuclear complexes $M(CO)_5$.

Mechanistic studies of transition-metal clusters are necessary to test the hypothesis that adjacent metal centers may lead to modes of reaction not found in mononuclear complexes.[1-6] Important questions about the mechanism, such as whether metal-metal bond cleavage occurs, can be answered by careful kinetics studies. The most thoroughly studied cluster system is the substitution reactions of $Ir_4(CO)_{12}$ and its substituted derivatives.[7-11] The reactivity was strongly influenced by the ligands on the cluster. For $Ir_4(CO)_{11}L$ and $Ir_4(CO)_{10}L_2$ the donor ability of the ligand L was important to the reactivity while for $Ir_4(CO)_9L_3$ and $Ir_4(CO)_8L_4$ the size of L became predominant.[8-11] Both of these effects are found in mononuclear complexes. Only in the substitution reactions of $Ir_4(CO)_{12}$ which proceeded primarily through a mechanism dependent on the entering ligand did a difference from mononuclear reactions appear.[7]

Darensbourg and Incorvia have investigated the reactions of $P(OMe)_3$ substituted derivatives of $Co_4(CO)_{12}$.[12-13] Reaction of the mono-substituted complex $Co_4(CO)_{11}P(OMe)_3$ with $P(OMe)_3$ proceeded by a second-order reaction, while reaction of the bis complex $Co_4(CO)_{10}(P(OMe)_3)_2$ with $P(OMe)_3$ to give $Co_4(CO)_9(P(OMe)_3)_3$ was first order in $Co_4(CO)_{10}(P(OMe)_3)_2$ and independent of $P(OMe)_3$.[12,13]

Candlin and Shortland studied CO substitution of $Ru_3(CO)_{12}$ by PPh_3, PPh_2Et, $PPhEt_2$, PBu_3, and PPh_3 (eq 1).[14] These reactions were reported to give only the

$$Ru_3(CO)_{12} + 3L \rightarrow Ru_3(CO)_9L_3 + 3CO \qquad (1)$$

tris-substituted complex with no evidence of the mono- or bis-substituted species.[14] The rate law observed was of the form

$$\text{rate} = \{k_1 + k_2[L]\}[Ru_3(CO)_{12}]$$

very similar to that observed for mononuclear species such as $Mo(CO)_6$.[14,15] Significantly, $Ru(CO)_4PPh_3$ did not yield $Ru_3(CO)_9(PPh_3)_3$ under conditions where CO was known to dissociate from $Ru(CO)_4PPh_3$.[14] CO dissociation from the intact triruthenium complex was suggested as the mechanism for reaction.[14] Subsequent work has confirmed these observations and shown that during reaction with PPh_3 the dissociation of CO is accelerated from $Ru_3(CO)_{11}PPh_3$ and $Ru_3(CO)_{10}(PPh_3)_2$ with respect to $Ru_3(CO)_{12}$.[16-20]

Reaction of the iron and osmium analogues with phosphines have also been reported.[21,22] For the osmium

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[†] Dedicated to the memory of Earl Muetterties, a dedicated scientist, mentor, and friend.

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