102649-08-1; $[NBu_4]_2[Pt_2(\mu\text{-}I)_2(C_6F_5)_4]$, 74436-18-3; $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6Cl_5)_4]$, 86392-08-7.

Supplementary Material Available: Listings of the final atomic coordinates and temperature factors for $[NBu_4]_2{}^+[Pt(C_6Cl_5)_4]^{2-}\cdot 2CH_2Cl_2$ (1) (Tables A and B, respectively), for $[NBu_4]^+[Pt(C_6Cl_5)_4]^-$ (2) (Tables C and D, respectively), and for $[NBu_4]^+[Pt(C_6Cl_5)_4NO]^-$ (3) (Tables E and F, respectively) and a listing of structure factors for 3 (Table G) (13 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Cis and Trans Dicarbonyl Derivatives of Platinum(II)

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Direct carbonylation of *cis*-$[Pt(C_6X_5)_2(OC_4H_8)_2]$ (X = F (1), Cl (2)) with CO (room temperature, $P_{CO} \approx 1$ atm) gives *cis*-$[Pt(C_6X_5)_2(CO)_2]$ (X = F (3), Cl (4)) as white, stable solids. The synthesis of *trans*-$[Pt(C_6F_5)_2(CO)_2]$ (5) by carbonylation of $(NBu_4)[$*trans*-$Pt(C_6F_5)_2Cl(CO)]$ in the presence of $AgClO_4$ is also described. Addition of neutral or anionic ligands to dichloromethane solutions of 3, 4, or 5 results in substitution of one CO group and affords *cis*- or *trans*-$[Pt(C_6X_5)_2L(CO)]^{n-}$ (n = 0, 1).

Introduction

Although the chemistry of the Pt(II) carbonyl derivatives has been fairly well developed and a wide range of compounds has been prepared and studied,[1] only a few Pt(II) dicarbonyls have been described, i.e., *cis*-$[PtX'_2(CO)_2]$ (X′ = Cl,[2a–f] Br,[2d] I[2d]), which are usually synthesized by high-pressure (40–210 atm) carbonylation of different substrates and *trans*-$[PtCl_2(CO)_2]$[3] (prepared at −80 °C and normal pressure). Only the cis dichloro derivative has been studied in detail.[4]

In this paper, we report the syntheses of *cis*-$[Pt(C_6X_5)_2(CO)_2]$ (X = F, Cl) and *trans*-$[Pt(C_6F_5)_2(CO)_2]$, at room temperature and normal pressure, as well as their reactions with both neutral and anionic ligands, which lead to two series of cis or trans monocarbonyl platinum(II) derivatives.

The synthesis of the *cis*-$[Pt(C_6X_5)_2(CO)_2]$ has already been briefly communicated.[5]

Results and Discussion

(a) Synthesis of *cis*-$[Pt(C_6X_5)_2(OC_4H_8)_2]$ (X = F (1), Cl (2)). Our aim has been to synthesize suitable precursors containing *two* readily displaceable ligands, thus allowing the simultaneous entrance of two groups of our choice under very mild reaction conditions. Since platinum(II) is a class b cation, an O-donor ligand would be ideal.[6] We attempted the preparation of compounds of the type $PtR_2(O\text{-donor})_2$, which could be achieved by halide abstraction from the binuclear $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6X_5)_2]_2$ complex (X = F,[7] Cl[8]), according to eq 1.

$$(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6X_5)_2]_2 + 2AgClO_4 \xrightarrow{THF} 2NBu_4ClO_4 + 2AgCl + 2cis\text{-}[Pt(C_6X_5)_2(OC_4H_8)_2] \quad (1)$$
$$\mathbf{1},\ X = F \qquad \mathbf{2},\ X = Cl$$

For our purposes, it was sufficient to obtain stable solutions of the precursors; notwithstanding, both complexes 1 and 2 can be isolated in 93% and 50% yields, respectively, in the form of white, air- and moisture-stable solids, at room temperature. This is fortunate, since solutions in any solvent of our choice can be prepared. At present we are engaged in a general study of the reactivity of both complexes.

(b) Synthesis of *cis*-$[Pt(C_6X_5)_2(CO)_2]$ (X = (3), Cl (4)). Bubbling CO, at room temperature and normal pressure, through dichloromethane solutions of 1 or 2 causes the substitution of two CO groups for the THF ligands, according to eq 2.

$$cis\text{-}[Pt(C_6X_5)_2(OC_4H_8)_2] \xrightarrow{CO} cis\text{-}[Pt(C_6X_5)_2(CO)_2] + 2OC_4H_8 \quad (2)$$
$$\mathbf{3},\ X = F \qquad \mathbf{4},\ X = Cl$$

Table I gives analytical and other data for both dicarbonyl complexes 3 and 4, which are indefinitely air- and moisture-stable white solids as are their solutions in noncoordinating solvents. Even recrystallization from diethyl

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Table I. Analytical Results (Calculated Values in Parentheses) and Other Characteristic Data

		C	H	N	M_r	Λ_M, Ω^{-1} cm^2 mol^{-1}	mp, °C
1	*cis*-$[\mathrm{Pt(C_6F_5)_2(THF)_2}]$	35.5 (35.7)	2.4 (2.4)		562 (673.3)		139 dec
2	*cis*-$[\mathrm{Pt(C_6Cl_5)_2(THF)_2}]$	28.9 (28.7)	1.9 (1.9)		796 (837.8)		144 dec
3	*cis*-$[\mathrm{Pt(C_6F_5)_2(CO)_2}]$	28.6 (28.7)			625 (585.2)		205 subl^a
4	*cis*-$[\mathrm{Pt(C_5Cl_5)_2(CO)_2}]$	22.4 (22.4)			*c*		208 dec^a
5	*trans*-$[\mathrm{Pt(C_6F_5)_2(CO)_2}]$	28.8 (28.7)			*c*		167 subl^b
6	*cis*-$[\mathrm{Pt(C_6F_5)_2py(CO)}]$	33.7 (34.0)	0.7 (0.8)	2.3 (2.2)	675 (636.3)		148
7	*cis*-$[\mathrm{Pt(C_6F_5)_2(PPh_3)(CO)}]$	45.9 (45.4)	2.1 (1.8)		810 (819.5)		174 dec
8	*cis*-$[\mathrm{Pt(C_6Cl_5)_2(PPh_3)(CO)}]$	37.8 (37.8)	1.7 (1.5)		994 (984.1)		189 dec
9	$(\mathrm{PPN})[$*cis*-$\mathrm{Pt(C_6F_5)_2Cl(CO)}]$	51.6 (52.0)	2.5 (2.7)	1.4 (1.2)		95	128
10	$(\mathrm{NBu_4})[$*cis*-$\mathrm{Pt(C_6F_5)_2Cl(CO)}]$	41.6 (41.7)	4.0 (4.3)	1.8 (1.7)		95	162
11	$(\mathrm{PPh_3Et})[$*cis*-$\mathrm{Pt(C_6F_5)_2Br(CO)}]$	42.7 (42.7)	2.3 (2.2)			97	107
12	$(\mathrm{PPh_2Me_2})[$*cis*-$\mathrm{Pt(C_6Cl_5)_2I(CO)}]$	30.2 (30.4)	1.4 (1.5)			101	174
13	*trans*-$[\mathrm{Pt(C_6F_5)_2py(CO)}]$	34.0 (34.0)	0.8 (0.8)	2.3 (2.2)	652 (636.3)		124
14	$(\mathrm{PPh_3Et})[$*trans*-$\mathrm{Pt(C_6F_5)_2Br(CO)}]$	43.1 (42.7)	2.3 (2.1)			91	136 dec
15	$(\mathrm{PPh_2Me_2})[$*trans*-$\mathrm{Pt(C_6F_5)_2I(CO)}]$	36.3 (36.0)	1.9 (1.7)			96	143 dec

^{a}Heating rate = 5 deg/min. ^{b}Heating rate = 1.25 deg/min. ^{c}The compound is not soluble enough.

Table II. IR Absorptions (cm^{-1}) of Structural Interest

		ν(CO)	X sensitive	$\nu(\mathrm{M{-}C_R})$ (R = $\mathrm{C_6Cl_5}$)	ν(M–X)	ref
1	*cis*-$[\mathrm{Pt(C_6F_5)_2(THF)_2}]$		818, 806			
2	*cis*-$[\mathrm{Pt(C_6Cl_5)_2(THF)_2}]$		*a*	637^b, 631		
	cis-$[\mathrm{PtCl_2(CO)_2}]$	2179, 2136			374, 352	13
3	*cis*-$[\mathrm{Pt(C_6F_5)_2(CO)_2}]$	2174, 2143	804, 792^b			
	cis-$[\mathrm{PtBr_2(CO)_2}]$	2164^c, 2122^c			252, 236	13
4	*cis*-$[\mathrm{Pt(C_6Cl_5)_2(CO)_2}]$	2160, 2126	847, 842	629^b, 623		
	trans-$[\mathrm{PtCl_2(CO)_2}]$	2150			*d*	3
5	*trans*-$[\mathrm{Pt(C_6F_5)_2(CO)_2}]$	2151	790			
6	*cis*-$[\mathrm{Pt(C_6F_5)_2py(CO)}]$	2112	806, 799			
7	*cis*-$[\mathrm{Pt(C_6F_5)_2(PPh_3)(CO)}]$	2112	801, 788			
8	*cis*-$[\mathrm{Pt(C_6Cl_5)_2(PPh_3)(CO)}]$	2100	840, 831	624, 607		
9	$(\mathrm{PPN})[$*cis*-$\mathrm{Pt(C_6F_5)_2Cl(CO)}]$	2089	803, 794		309	
10	$(\mathrm{NBu_4})[$*cis*-$\mathrm{Pt(C_6F_5)_2Cl(CO)}]$	2092	803, 798		301	
11	$(\mathrm{PPh_3Et})[$*cis*-$\mathrm{Pt(C_6F_5)_2Br(CO)}]$	2090	800, 793			
12	$(\mathrm{PPh_2Me_2})[$*cis*-$\mathrm{Pt(C_6Cl_5)_2I(CO)}]$	2080, 2052^e	840^b, 836	623, 616		
13	*trans*-$[\mathrm{Pt(C_6F_5)_2py(CO)}]$	2112	808			
	$(\mathrm{NBu_4})[$*trans*-$\mathrm{Pt(C_6F_5)_2Cl(CO)}]$	2084	797^f, 779			11
14	$(\mathrm{PPh_3Et})[$*trans*-$\mathrm{Pt(C_6F_5)_2Br(CO)}]$	2112	793^f, 780			
15	$(\mathrm{PPh_2Me_2})[$*trans*-$\mathrm{Pt(C_6F_5)_2I(CO)}]$	2082	793^f, 779			

^{a}A strong and broad absorption of ligand THF at 840 cm^{-1} precludes an accurate assignation in this case. ^{b}Shoulder. ^{c}Registered in $\mathrm{C_6H_6}$ solution. ^{d}Not determined in the original reference. ^{e}In $\mathrm{CH_2Cl_2}$ solution only a single absorption at 2084 cm^{-1} is observed. ^{f}Very weak absorption.

ether causes no alteration, while more basic ethers such as tetrahydrofuran partially displace one of the two CO groups as can be observed by IR monitoring of the THF solutions. For X = F, a band at lower energies (characteristic of a monocarbonyl) is present in the freshly prepared solutions, while for X = Cl, only after 2 h a similar band becomes perceptible. After 3 days, however, the original IR pattern due to the dicarbonyl species is present; albeit its intensity is decreased.

On the other hand, complexes **3** and **4** show remarkable thermal stability: **3** sublimes at 205 °C and **4** decomposes at 208 °C. In contrast with the thermal stability of **3** and **4**, the other, so far reported, Pt(II) dicarbonyl derivatives *cis*-$[\mathrm{PtX'_2(CO)_2}]$ (X′ = Cl, Br, I) readily dissociate a CO group to give polynuclear derivatives, according to eq 3.

$$2cis\text{-}[\mathrm{PtX'_2(CO)_2}] \rightleftarrows 2\mathrm{CO} + [\mathrm{Pt}(\mu\text{-}\mathrm{X'})\mathrm{X'(CO)}]_2 \quad (3)$$

For instance, solid *cis*-$[\mathrm{PtCl_2(CO)_2}]$ under vacuum or under nitrogen atmosphere evolves CO to give $[\mathrm{Pt}(\mu\text{-}\mathrm{Cl})\mathrm{Cl(CO)}]_2$ and $\mathrm{Pt_2Cl_4(CO)_3}$. It can be stored under CO atmosphere, in order to shift the equilibrium 3 to the left.

(c) IR Spectra of Complexes 1–4. It is possible to assign a cis structure to complexes **1**–**4** by evaluating their IR spectra (Table II).

The IR spectra of the two dicarbonyl complexes **3** and **4** show two ν(CO) absorptions (C_{2v}, $A_1 + B_1$). The spectra of the two pentafluorophenyl complexes **1** and **3** show two absorptions due to the X-sensitive modes of the $\mathrm{C_6F_5}$ groups, which must therefore be mutually cis.[9] Analogously, the spectra of the two pentachlorophenyl complexes **2** and **4** show two absorptions assignable to ν(Pt–C).[10] The spectrum of complex **4** also has two absorptions (847 (m), 842 (m) cm^{-1}) due to the X-sensitive modes of the $\mathrm{C_6Cl_5}$ groups,[9b] while the corresponding absorptions for **2** cannot be assigned because of the strong and broad absorption at 840 cm^{-1} due to the $\mathrm{OC_4H_8}$ ligand. Interestingly, the higher ν(CO) absorptions observed in the IR spectra of **3** and **4** (2179, 2174 cm^{-1}) lie unusually high in comparison with other metal carbonyls, emphasizing that (a) no π-back-bonding is operative (or should be negligible) in these complexes and (b) stable Pt(II)–CO bonds can be formed despite the lack of any substantial π-contribution.

(d) Synthesis of *trans*-$[\mathrm{Pt(C_6F_5)_2(CO)_2}]$ (5). In view of the above results the preparation of the isomeric trans dicarbonyls was of considerable interest in order to compare their stability and properties.

So, *trans*-$[\mathrm{Pt(C_6F_5)_2(CO)_2}]$ (**5**) can be synthesized by treating $(\mathrm{NBu_4})[$*trans*-$\mathrm{Pt(C_6F_5)_2Cl(CO)}]$[11] with $\mathrm{AgClO_4}$ and subsequent carbonylation (eq 4; see Experimental Section).

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Table III. ^{19}F NMR Parameters of Some Monocarbonyl Complexes (Cis and Trans Isomers)[a,b]

complex	δ(*o*-F)	δ(*m*-F)	δ(*p*-F)	^3J(Pt–*o*-F)
cis-[Pt(C_6F_5)$_2$py(CO)] (6)	−119.7*, −122.2	−163.7, −164.4	−159.3, −160.4*[c]	399, 366
trans-[Pt(C_6F_5)$_2$py(CO)] (13)	−121.5	−162.8	−158.9	247
(NBu_4)[*cis*-Pt(C_6F_5)$_2$Cl(CO)] (10)	−119.4*, −119.7	−165.6, −165.8	−162.8, −162.9	429, 374
(NBu_4)[*trans*-Pt(C_6F_5)$_2$Cl(CO)][d]	−119.6	−165.1	−162.6	256
(PPh_3Et)[*cis*-Pt(C_6F_5)$_2$Br(CO)] (11)	~−119.2[e]	−165.5, −166.1	−163.0*[f], −163.5	~388, ~414
(PPh_3Et)[*trans*-Pt(C_6F_5)$_2$Br(CO)] (14)	−118.8	−165.3	−162.9	257
cis-[Pt(C_6F_5)$_2$(PPh_3)(CO)] (7)	~−119.2, ~−119.4*[g,h]	−163.6[h], −164.3	−159.8, −159.9	~316, ~352

[a] The assignments of the signals to each of the two inequivalents C_6F_5 groups on the cis isomers are made, when possible, on the assumption that the C_6F_5 group trans to the ligand with the lower trans influence should show higher coupling constants to platinum. Signals marked with an asterisk are assigned to the C_6F_5 group trans to CO. [b] Chemical shift in ppm, reference $CFCl_3$; coupling constants in Hz. [c] Coupling to Pt is observed: $^5J_3$(Pt–*p*-F) = 19 Hz. [d] Reported in ref 11. [e] Chemical shifts of both types of *o*-F are almost coincident, but the coupling constant ^3J(Pt–*o*-F) is different for each of them. [f] ^5J(Pt–*p*-F) = 19 Hz). [g] Overlap of both signals allows only an approximate assignation. [h] Coupling to P is observed.

Unfortunately the suitable similar precursor (NBu_4)[*trans*-Pt(C_6Cl_5)$_2$Cl(CO)] has as yet not bee reported.

$$(NBu_4)[trans\text{-}Pt(C_6F_5)_2Cl(CO)] + AgClO_4 + CO \rightarrow AgCl + NBu_4ClO_4 + trans\text{-}[Pt(C_6F_5)_2(CO)_2] \quad (4)$$

Complex **5** is an air- and moisture-stable, white solid which sublimes at 167 °C, giving a mixture of the cis (**3**) and trans (**5**) isomers. In solution it slowly (~5 days, at room temperature in CH_2Cl_2) isomerizes to the more stable cis isomer **3**. In agreement with the trans geometry (D_{2h}) assigned to **5**, its IR spectrum shows a single band due to ν(CO) (B_{1u}) along with one band due to the X-sensitive mode of the C_6F_5 group[9] (Table II).

The trans–cis isomerization takes place much more readily for the less stable *trans*-[$PtCl_2(CO)_2$] complex (complete after 24 h, room temperature).

(e) Substitution Reactions of 3, 4, and 5. Addition of neutral or anionic ligands to dichloromethane solutions of the dicarbonyls **3**, **4**, or **5** causes the displacement of one CO group and leads to the formation of monocarbonyl derivatives, according to eq 5 and 6.

$$cis\text{-}[Pt(C_6X_5)_2(CO)_2] + L^{n-} \xrightarrow[-CO]{} \underset{\mathbf{6\text{–}12}}{[cis\text{-}Pt(C_6X_5)_2L(CO)]^{n-}} \quad (5)$$

$n = 0$: X = F, L = py (**6**); X = F, L = PPh_3 (**7**); X = Cl, L = PPh_3 (**8**)

$n = 1$: X = F, L = Cl (**9**); X = F, L = Br (**11**); X = Cl, L = I (**12**)

$$trans\text{-}[Pt(C_6F_5)_2(CO)_2] + L^{n-} \xrightarrow[-CO]{} \underset{\mathbf{13\text{–}15}}{[trans\text{-}Pt(C_6F_5)_2L(CO)]^{n-}} \quad (6)$$

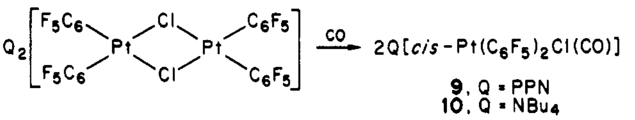
$n = 0$: L = py (**13**)

$n = 1$: L = Br (**14**), I (**15**)

In the region 2112–2082 cm^{-1} all the monocarbonyl derivatives show IR absorptions due to ν(CO) readily discernible from the bands due to the dicarbonyl derivatives. The course of these substitution reactions can also easily be followed by monitoring the IR spectra in the ν(CO) region. The substitution is very rapid for compounds **3** and **5**, while the pentachlorophenyl compound **4** is much more inert, 48 h being necessary to obtain almost complete disappearance of the dicarbonyl signals.

The IR spectra of these monocarbonyl derivatives do not permit us to assign unequivocally the cis or trans geometry of the complexes. In fact, group theory predicts the same number of IR-active vibrations for the X-sensitive modes for the C_6F_5[9] or C_6Cl_5[9b,10] in the cis (C_s, 2 A′) or in the trans (C_{2v}, $A_1 + B_1$) complexes. In practice the spectra of all the complexes (**6**–**12**) obtained from the cis derivatives *cis*-Pt(C_6X_5)$_2$(CO)$_2$ (X = F (**3**), Cl (**4**)) show a similar pattern due to the X-sensitive mode of the C_6X_5 groups[9,10] (two strong absorptions) while in complexes **13**–**15** obtained from *trans*-Pt(C_6F_5)$_2$(CO)$_2$ (**5**) these absorptions have very different intensities, one of them being very weak or unperceptible (see Table II).

The ^{19}F NMR spectra allow an inequivocal structural assignment since the [*cis*-Pt(C_6F_5)$_2$L(CO)]$^{n-}$ complexes contain two inequivalent C_6F_5 groups which are equivalent in the trans isomers. Table III collects some ^{19}F NMR data which confirm that these substitution reactions take place with stereoretention. This structural assignation is in agreement with two other facts. (a) The ν(Pt–Cl) in [*trans*-Pt(C_6F_5)$_2$ClCO]$^-$ appears at higher frequencies (330 cm^{-1}) than that observed for the cis isomer (300 cm^{-1}) (see Table II), as a consequence of the higher trans influence of the C_6F_5 group. (b) Complex **9** can also be obtained by cleavage of the bridges in Q_2[Pt(μ-Cl)(C_6F_5)$_2$]$_2$, according to eq 7



(7)

Substitution of one CO group in the dicarbonyl derivatives shifts the ν(CO) band toward lower frequencies; the observed shift is greater for anionic substituents than for neutral ones, in agreement with numerous previous observations for similar cases.[12]

The monocarbonyl complexes **6**–**15** bind their CO ligand strongly; thus, the intensity of the ν(CO) band in complex **7** does not decrease by 3 h of refluxing in toluene containing an excess of PPh_3, and the action of an excess of pyridine (72 h, room temperature followed by 16 h of refluxing) in complex **6** is also ineffective. The action (~170 h) of pyridine on *trans*-[Pt(C_6F_5)$_2$py(CO)] (**13**) at room temperature in a CH_2Cl_2 solution only causes some perceptible (IR) isomerization to the cis derivative.

It is possible to displace both CO groups in the dicarbonyl *cis*-[Pt(C_6F_5)$_2$(CO)$_2$] (**3**) by reaction with bidentate ligands, according to eq 8.

$$cis\text{-}[Pt(C_6F_5)_2(CO)_2] + L\text{-}L \rightarrow 2CO + cis\text{-}[Pt(C_6F_5)_2(L\text{-}L)] \quad (8)$$

L-L = dppm (bis(diphenylphosphino)methane), 2,2′-bpy (2,2′-bipyridine)

The 1:1 reaction of **3** with dppm occurs instantaneously, while the reaction with 2,2′-bpy requires about 3 days. IR

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Table IV. Experimental Conditions To Synthesize Monocarbonyl Compounds[a]

$[Pt(C_6X_5)_2(CO)_2] + L^{n-} \rightarrow [Pt(C_6X_5)_2L(CO)]^{n-}$

reactn product	substr	nucleophile	reactn time	crystallizatn mixture	yield, %
6	3 (0.1 g, 0.17 mmol)	py (17 μL, 0.21 mmol)		CH_2Cl_2/*n*-hex	74
7	3 (82 mg, 0.14 mmol)	PPh_3 (37 mg, 0.14 mmol)		CH_2Cl_2/*n*-hex	96
8	4 (0.1 g, 0.13 mmol)	PPh_3 (45 mg, 0.17 mmol)	48 h	Et_2O/*n*-hex	86
9	3 (0.11 g, 0.18 mmol)	PPNCl (0.1 g, 0.18 mmol)		Et_2O/*n*-hex	93
11	3 (0.1 g, 0.17 mmol)	PPh_3EtBr (67 mg, 0.18 mmol)		CH_2Cl_2/*n*-hex	95
12	4 (0.15 g, 0.19 mmol)	PPh_2Me_2I (65 mg, 0.19 mmol)	48 h	Et_2O/*n*-hex	76
13	5 (0.1 g, 0.17 mmol)	py (14 μL, 0.17 mmol)		CH_2Cl_2/*n*-hex	92
14	5 (0.1 g, 0.17 mmol)	PPh_3EtBr (67 mg, 0.17 mmol)		CH_2Cl_2/*n*-hex	95
15	5 (0.1 g, 0.17 mmol)	PPh_2Me_2I (59 mg, 0.17 mmol)		Et_2O/*n*-hex	92

[a] If not expressed, the reaction takes place instantaneously.

monitoring of this reaction permits the detection of a decreasing presence of the starting product, but the presence of a monocarbonyl intermediate cannot be verified.

Experimental Section

C, H, and N analyses were made with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded over the 4000–200 cm^{-1} range on a Perkin-Elmer 599 spectrophotometer, using Nujol mulls between polyethylene sheets. The ^{19}F NMR spectra were recorded on a Varian XL-200 in $CDCl_3$ solutions. Molecular weights were determined in $CHCl_3$ solution with a Knauer digital osmometer. Molar conductivities were determined in 5×10^{-4} M acetone solutions with a Philips PW 9509 conductimeter, using a PW 9510 cell. The sublimation or decomposition points for complexes 3, 4, and 5 were determined with a thermogravimetric system Perkin-Elmer TGS-2. Decomposition points of the other complexes were determined with a Büchi, Mod. Dr. Tottoli apparatus.

Complexes $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (X = F,[7] Cl[8]) and (NBu_4)[*trans*-$Pt(C_6F_5)_2Cl(CO)$][11] were prepared as previously described. The carbonylation reactions were conducted at room temperature and atmospheric pressure; the reactions with silver salts were carried out under exclusion of light.

(a) *cis*-$[Pt(C_6F_5)_2(OC_4H_8)_2]$ (1). To a freshly distilled tetrahydrofuran solution (20 mL) of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (1.5 g, 0.93 mmol) under nitrogen atmosphere was added 0.385 g (1.86 mmol) of $AgClO_4$. [We have not found any problem with these solutions; however, the usual cautions should be adopted on evaporating the perchlorato-containing solutions.] After 20 min of stirring, the suspension was evaporated to dryness and the residue was extracted with 50 mL of diethyl ether from the insoluble residue (AgCl + NBu_4ClO_4). The clear solution was vacuum concentrated to ca. 5 mL, and 20 mL of *n*-hexane was added. A white solid precipitated (1, 1.16 g, 93% yield).

(b) *cis*-$[Pt(C_6Cl_5)_2(OC_4H_8)_2]$ (2). Following the procedure described above, 0.68 g (0.35 mmol) of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6Cl_5)_2]_2$ and 0.145 g (0.7 mmol) of $AgClO_4$ were reacted. The resulting yellow solid was recrystallized from OC_4H_8/*n*-hexane to obtain 2 as a white solid (0.3 g, 50% yield).

(c) *cis*-$[Pt(C_6X_5)_2(CO)_2]$ (X = F (3), Cl (4)). Bubbling CO through a CH_2Cl_2 solution (10 mL) of 1 (0.52 mmol) or 2 (0.23 mmol) for 20 min gave a white solid (3, 0.24 g, 79% yield, or 4, 0.16 g, 91% yield).

(d) *trans*-$[Pt(C_6F_5)_2(CO)_2]$ (5). To a THF solution of 0.51 g (0.61 mmol) of (NBu_4)[*trans*-$Pt(C_6F_5)_2Cl(CO)$] was added 0.127 g (0.61 mmol) of $AgClO_4$. After 20 min of stirring the mixture was evaporated to dryness and the residue was extracted with diethyl ether (20 mL). The insoluble AgCl and NBu_4ClO_4 were filtered. Vacuum evaporation of the filtrate gave an oil which was dissolved in 10 mL of CH_2Cl_2. Bubbling CO through this solution caused the precipitation of a white solid (5, 0.28 g, 80% yield).

A dichloromethane solution (20 mL) of 5 (30 mg, 0.051 mmol) was stirred at room temperature for 5 days. Evaporation to dryness and subsequent treatment of the residue with *n*-hexane gave complex 3 (23 mg, 77% yield).

(e) Monocarbonyl Complexes 6–9 and 11–15. To a dichloromethane solution (20 mL) of the corresponding substrates (3, 4, and 5, respectively) was added an equimolecular amount of the ligand L. The mixture was stirred and evaporated to dryness, and the resulting residue was dissolved in CH_2Cl_2 or Et_2O (see Table IV) and crystallized by slow diffusion of *n*-hexane at −30 °C. Table IV collects pertinent informations for each case.

(f) (NBu_4)[*cis*-$Pt(C_6F_5)_2Cl(CO)$] (10). Through a dichloromethane solution (15 mL) of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.2 g, 0.12 mmol) at room temperature was passed CO for 10 min. The mixture was evaporated to dryness, and the obtained residue was dissolved in 2-PrOH (3 mL). By careful overlaying with *n*-hexane (20 mL) and after slow diffusion, colorless crystals of 10 (0.16 g, 50% yield) were obtained.

The same procedure using $(PPN)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ as starting product gave complex 9 in 86% yield.

(g) Reactions of 3 with Bis(diphenylphosphino)methane or 2,2′-Bipyridine. To a dichloromethane solution (20 mL) of complex 3 (50 mg, 0.085 mmol) was added dppm (33 mg, 0.085 mmol). Both CO groups are instantaneously displaced. Evaporation to dryness and washing with diethyl ether gave $[Pt(C_6F_5)_2(dppm)]$[14] (57 mg, 74% yield).

Addition of 2,2′-bpy (26.5 mg, 0.17 mmol) to a dichloromethane solution (20 mL) of complex 3 (100 mg, 0.17 mmol) caused the slow substitution (3 days) of both CO groups. Workup as above gave $[Pt(C_6F_5)_2(bpy)]$[15] (100 mg, 86% yield).

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