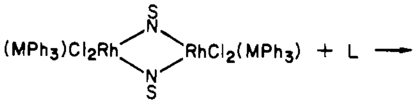
a band in the region 1610–1630 cm^{-1} due to ν_{NO} and the appearance of a new band at 840 cm^{-1} indicate the replacement of the nitrosyl group by NS. It may be noted that the difference between the 1620 and 840 cm^{-1} is of the same order as that between nonbridging and bridging NO groups. For the two bridging groups the NS frequencies will be very close together and may be superimposed.

In order to prove further the bridging nature of the NS group we have carried out reactions of I and II with PPh_3 and $AsPh_3$ which resulted in the bridge cleavage (eq 1). The IR



$$2[Rh(NS)Cl_2(MPh_3)L] \quad (1)$$

III: M = P, L = PPh_3
IV: M = P, L = $AsPh_3$
IV: M = As, L = PPh_3
V: M = As, L = $AsPh_3$

spectra of these complexes show absorption band in the region 1116–1120 cm^{-1} which are in close agreement with the values reported previously for similar complexes. This supports that the band at 840 cm^{-1} in complexes I and II, which disappeared in the spectra of complexes III–V, is a characteristic band of bridging thionitrosyl groups. Similar results are observed in iridium nitrosyl complexes,[19] but in contrast to Rh and IR complexes, $[M(NO)X_3(PPh_3)_2]$ (M = Ru, Os; X = Cl, Br) show no reaction with $NSCl(solvent)_x$. The reactions of $NSCl(THF)_x$ with the neutral complexes $[(\eta^5\text{-}C_5H_5)M(CO)_2(NO)]$ (M = Cr or Mo) in THF or CH_2Cl_2 afforded $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ and $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl]_2$.[8]

On the basis of these reactions, we conclude that the NO group is replaced by the NS group in metal–nitrosyl complexes having low frequencies (ν_{NO} = 1500–1650 cm^{-1}).

Registry No. I, 76136-88-4; II, 76136-89-5; III, 76136-90-8; IV, 76136-91-9; V, 76136-92-0; $(NSCl)_3$, 5964-00-1; $Rh(NO)(PPh_3)_3$, 21558-94-1; $Rh(NO)Cl_2(AsPh_3)_2$, 27411-16-1.

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Syntheses of Carbonyl Halides of Late Transition Elements in Thionyl Chloride as Solvent. Carbonyl Complexes of Palladium(II)

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Palladium has been extensively used as a catalyst of several reactions involving CO such as the snythesis of dialkyl oxalates,[1] alkyl isocyanates from nitro aromatics,[2] and esters from olefins and alcohols.[3] In spite of this, the chemistry of halo–carbonyl complexes of palladium is still far from a complete understanding. An earlier report by Manchot and König[4] described a compound of analytical composition $PdCl_2(CO)$ obtained by carbonylation of $PdCl_2$ in methanol; this formulation was later questioned[5] and the product was suggested to be $[PdCl(CO)]_n$ contaminated with $PdCl_2$. A carbonyl absorption at 1976 cm^{-1} was measured[6] for the product reported by Manchot and König, and a strong absorption at 1947 cm^{-1} was recently reported[7] for $PdCl_2(CO)(PhCN)$. However, these values are unusually low for terminal carbonyl groups of late transition elements and they are not in agreement with the values reported[6] for $Pt_2Cl_4(CO)_2$, for *cis*-$PtCl_2(CO)_2$ (2177 and 2136 cm^{-1} in thionyl chloride as solvent), and for some cationic carbonyl complexes of palladium(II), which were found[9] to absorb around 2140 cm^{-1}. On the basis of the surprisingly low values of ν_{CO} reported[6] by Irving and Magnusson, a stronger π back-donation was suggested for palladium(II) in comparison with platinum(II).[10] A proposal was also offered[11] that the palladium compound might be dimeric as its platinum analogue was suggested[6] to be, but with carbonyl bridges rather than chloride bridges, an unprecedented feature for unsubstituted halometal carbonyls.[12]

Table I. IR Carbonyl Stretching Vibrations of Carbonyl Complexes of Palladium(II) and Platinum(II)

	$\tilde{\nu}_{CO}$, cm^{-1}				
compd	cyclohexane	C_6H_6	CH_2Cl_2	Nujol	ref
$Pd_2Cl_4(CO)_2$	2159	2162	2166	2167	this work
$Pt_2Cl_4(CO)_2$	2128	2129	2139	2146	this work
				2146	6
$[PdCl_3(CO)]^-$			2146	2141	this work
			2132		20
$[PtCl_3(CO)]^-$		2105 (toluene)	2109		this work
				2106	21

We have recently discovered a new method for preparing halo carbonyls of gold(I) and platinum(II).[8,13] We want now to report that application of this method to $PdCl_2$ did in fact lead to genuine palladium(II)–halo–carbonyl derivatives.

Experimental Section

$PdCl_2$ of various origins gave similar results.

$Pd_2Cl_4(CO)_2$ was prepared by treating $PdCl_2$ with CO at super atmospheric pressure in thionyl chloride. In a typical experiment, $PdCl_2$ (3.1 g, 17.48 mmol) was introduced in a Hastelloy C autoclave together with $SOCl_2$ (20 mL) and stirred at about 120 °C for 12 h with CO under pressure (initial P_{CO} = 50 atm). The yellow-orange solution was filtered under a CO atmosphere, and the filtrate was added to heptane pretreated with some drops of thionyl chloride. The yellow-orange microcrystalline precipitate was briefly dried in a stream of CO and kept in vials sealed under CO (2.26 g, 63% yield). The compound is soluble in dichloromethane, thionyl chloride, and benzene (about 1%) and slightly soluble in saturated hydrocarbons. Under strictly anhydrous conditions it is reasonably stable either in the solid state or in solution at room temperature: decomposition occurred immediately upon contact with trace amounts of water, finally yielding a black precipitate, presumably palladium metal, through the intermediacy of unidentified orange solids. Anal. Calcd for $Pd_2Cl_4(CO)_2$

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($C_2Cl_4O_2Pd_2$): C, 5.85; Cl, 34.53; mol wt 410.6. Found: C, 6.0; Cl, 35.0; mol wt (cryoscopy in benzene) 432. The reaction of $PdCl_2$ with CO took place also at atmospheric pressure, as monitored by IR; however, the reaction was inconveniently slow.

The solution spectra of $Pd_2Cl_4(CO)_2$ are in Table I. Reliable Nujol mull spectra can be obtained only by careful drying of all the material used for the measurement: however, even under the most rigorous conditions carbonyl bands at lower wavenumbers due to hydrolytic products were observed in addition to that presented in Table I. The IR bands were regarded as genuinely attributable to the dimeric palladium compound only after observing their intensity behavior with time.

$NH_2Et_2[PdCl_3(CO)]$ was prepared from $Pd_2Cl_4(CO)_2$ and a stoichiometric amount of NH_2Et_2Cl in dichloromethane as solvent. To a solution of the carbonyl–chloro complex of palladium(II) (0.47 g, 1.14 mmol) in dichloromethane (20 mL) was added a solution of NH_2Et_2Cl (0.255 g, 2.33 mmol) in the same solvent (20 mL) in about 15 min. An IR spectrum of the resulting orange solution showed the absorption at 2146 cm^{-1}, due to the $[PdCl_3(CO)]^-$ anion. The solution was concentrated, and the compound precipitated by addition of *n*-heptane was filtered and dried in vacuo (0.59 g, 82% yield). Anal. Calcd for $C_5H_{12}Cl_3NOPd$: C, 19.07; H, 3.84; Cl, 33.77; N, 4.45. Found: C, 18.4; H, 4.0; Cl, 32.9; N, 4.4. In a gas volumetric control experiment it was found that the addition of the stoichiometric amount of NH_2Et_2Cl to the solution of $Pd_2Cl_4(CO)_2$ did not evolve any significant volume of gas. Use of excess NH_2Et_2Cl produced the precipitattion of the red $(NH_2Et_2)_2PdCl_4$ with simultaneous evolution of the expected volume of CO.

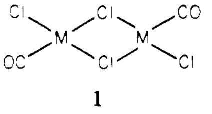
$Pt_2Cl_4(CO)_2$ was prepared from $PtCl_2(CO)_2$[8] by the following procedure. *cis*-Dichlorodicarbonylplatinum(II) (3 g) was stirred with concentrated HCl (10 mL) under a nitrogen atmosphere at room temperature for 12 h. To the resulting yellow solution was added thionyl chloride (70 ml) dropwise while the temperature was around 0 °C. When gas evolution had ceased, the $SOCl_2$ solution of the dimer was filtered, and heptane was added to it to decrease the solubility. The yellow-orange dichloro–carbonyl compound was collected by filtration and dried in vacuo. Satisfactory elemental analyses (C, Cl, CO) were obtained for the compound. The IR data for $Pt_2Cl_4(CO)_2$ are in Table I. Similar to the corresponding palladium analogue, reliable Nujol mull spectra are difficult to obtain, in view of the extreme reactivity with moisture and with the material of the IR windows. Germanium windows were finally used to retard the formation of spurious carbonyl bands at lower $\tilde{\nu}$.

Results and Discussion

The dichloro–carbonyl complex of palladium(II) was found to be the product of the carbonylation of $PdCl_2$ in thionyl chloride as solvent (eq 1). The compound has only one sharp

$$2PdCl_2 + 2CO \xrightarrow[120\ °C]{P_{CO} = 50\ atm} Pd_2Cl_4(CO)_2 \qquad (1)$$

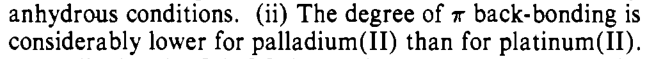
IR carbonyl absorption, which shows a slight solvent effect, as indicated from the data of Table I. The yields of the compound were around 60%, and no other soluble product was found to be present in the crude mixture of the reaction. In particular, although the preparation and the subsequent workup were carried out under CO, no IR evidence of a dicarbonyl derivative of palladium, similar to $PtCl_2(CO)_2$ was ever obtained. In view of the dimeric molecular weight in benzene and of the unique carbonyl stretching vibration in the infrared, the dimeric trans structure **1** should be assigned to



1

M = Pd, Pt

this compound (M = Pd). It is worth noting that the corresponding platinum(II) complex, $Pt_2Cl_4(CO)_2$, was also reported to show one single carbonyl stretching vibration, and a similar structure was assigned to it.[6] We have repeated the IR measurements in the carbonyl stretching region, substantially confirming the earlier result (see Table I). It now appears that Pd(II) and Pt(II) behave similarly, contrary to some earlier thoughts, as defined above, which were based on evidently erroneous data. As it is shown from the data of Table I, palladium(II) has a ***higher*** value of the $\tilde{\nu}_{CO}$ in comparison with the corresponding platinum(II) complex, in agreement with a quite general trend for metal carbonyl derivatives, showing a higher value of $\tilde{\nu}_{CO}$ for the 4d term of the same family of compounds in a vertical triad of elements.[14] The high value of $\tilde{\nu}_{CO}$ also confirms the generally scarse tendency of late transition elements to π back-donate in carbonyl complexes (i.e., Au(I),[8] Pt(II),[8] Cu(I)[15]). The reactions with the stoichiometric amount of PPh_3 transformed $Pd_2Cl_4(CO)_2$ into the products resulting from substitution and bridge splitting (eq 2 and 3). The assignment of structure to the monomeric[16] and the dimeric[17] products was made on the basis of the IR spectra, especially in the 250–400-cm^{-1} region typical of Pd–Cl vibrations. The 1:1 reaction with PPh_3, as monitored by gas volumetry under CO, was found to result in the evolution of the expected amount of CO, thus showing that the substitution of coordinated CO by PPh_3 in $Pd_2Cl_4(CO)_2$ occurs more readily than the bridge-splitting with retention of CO. We have thus found no evidence of the presence of any substantial amount of $PdCl_2(CO)PPh_3$ under the experimental conditions used for reaction 2. This is in agreement with the nonexistence[18] of $PdCl_2(CO)AsPh_3$ recently established under the experimental conditions of an earlier report[19] and contrasts with the behavior observed[8] with platinum(II) for which the monosubstituted carbonyl derivatives $PtCl_2(CO)L$ were found to exist. This difference may be related to the substantially nonexistent π-back-bonding properties of the CO ligand in palladium(II) (see Table I), the situation having no chance to improve with the π-bonder tertiary phosphine. One single absorption at 2056 cm^{-1} has been reported[6] for [PdCl(en)-CO][$PdCl_3$(CO)]. While the IR data of Table I for $[MCl_3(CO)]^{-3}$ are not in agreement with this value, which should therefore be regarded as spurious, our data are close to the 2132-cm^{-1} carbonyl band reported for a dichloromethane solution of $[PdCl_3(CO)]^-$.[20]



$$Pd_2Cl_4(CO)_2 + 4PPh_3 \longrightarrow 2CO + 2\,trans\text{—}PdCl_2(PPh_3)_2 \qquad (3)$$

In conclusion, this work has definitely established the following. (i) The existence of dimeric $Pd_2Cl_4(CO)_2$, that palladium(II) and platinum(II) form the same families of compounds $M_2Cl_4(CO)_2$ and $[MCl_3(CO)]^-$, and that no predominant reduction of palladium(II) occurs with CO under strictly anhydrous conditions. (ii) The degree of π back-bonding is considerably lower for palladium(II) than for platinum(II). Accordingly, the Pd–CO is much more reactive than the corresponding Pt–CO bond, as shown by the fact that $Pd_2Cl_4(CO)_2$ is observable only under anhydrous conditions and by the failure to observe any evidence of the monomeric $PdCl_2(CO)_2$. This is in agreement with the well-established use of palladium in catalytic reactions involving carbon monoxide.

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Registry No. $Pd_2Cl_4(CO)_2$, 75991-68-3; $Pt_2Cl_4(CO)_2$, 17522-99-5; $NH_2Et_2[PdCl_3(CO)]$, 75934-65-5; $[PtCl_3(CO)]^-$, 21710-57-6; $PdCl_2$, 7647-10-1; $PtCl_2(CO)_2$, 15020-32-3.

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Preparation of Tertiary Phosphine–Olefin Complexes of Platinum(0): A Convenient Synthesis of Ethylenebis(triethylphosphine)platinum(0)[1]

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and George M. Whitesides*

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Presently available synthetic routes to complexes of trialkylphosphines with platinum(0) involve starting materials which are not readily available,[4–6] difficult isolations,[7] and manipulations of air-sensitive materials.[4–8] The more convenient of these preparations entail displacement of cyclooctadiene from bis(cyclooctadiene)platinum(0), but this compound is prepared only in moderate yield (40–60%) by an inconvenient reaction.[9] One of the simplest members of the class of platinum(0)–phosphine complexes, ethylenebis(triethylphosphine)platinum(0) (**1**) has not been reported. We wish to report a convenient, high-yield preparation of **1** by thermal decomposition of the air-stable, crystalline complex diethylbis(triethylphosphine)platinum(II). The generality of this thermal decomposition reaction as a route to platinum(0)–phosphine complexes is examined briefly.

Experimental Section

General Information. Proton NMR spectra were recorded on a Bruker WM-250 instrument. $\{^1H\}^{31}P$ NMR spectra were obtained at 36.4 MHz on a modified Bruker HFX-90 or Jeol FX-90Q spectrometer. ^{31}P chemical shifts, in parts per million, are relative to external 85% phosphoric acid (downfield shifts positive). Mass spectra were recorded on a Varian MAT-44 spectrometer. Olefins were removed from cyclohexane by treatment with concentrated H_2SO_4, and the cyclohexane was washed with saturated $NaHCO_3$, dried over P_4O_{10}, and distilled under argon. Toluene-d_8 was passed through a 1 × 2 cm column of activated alumina and degassed by freeze–pump–thaw cycles. Ether was distilled under argon from sodium benzophenone dianion. Welding grade argon was used for inert-atmosphere work without further purification. Compounds were stored in a dessicator at −10 °C.

Diethyl- and dipropylbis(triethylphosphine)platinum(II) were prepared by modifications of literature methods.[10,11]

Dicyclobutylbis(triethylphosphine)platinum(II). Special care was needed in preparing the thermally unstable dicyclobutyl and dicyclopentyl compounds. In an argon-flushed 100-mL flask was suspended 0.50 g (1.3 mmol) of dichloro(1,5-cyclooctadiene)platinum(II)[10] ($(COD)PtCl_2$) in 40 mL of ether. To this mixture was added 10 mL of 0.53 M (5.3 mmol) cyclobutylmagnesium chloride by syringe at −50 °C. The solution was allowed to warm to −20 °C over 2 h and stirred at this temperature for 6 h. The entire reaction mixture was passed through a 1 × 6 cm column of silica gel containing 5% activated charcoal at −78 °C. The solution thus obtained was treated with 0.40 mL (2.8 mmol) of triethylphosphine at 0 °C. After 15 min the ether was partially removed under reduced pressure. Adding methanol (5 mL) and cooling to −78 °C induced crystallization. The white precipitate was separated by filtration and recrystallized from ether–methanol to give 0.40 g (56%) of fine needles, mp 87–88 °C. ^{31}P NMR: $\delta = 6.3$ ($J_{Pt,P} = 1647$ Hz).

Table I. Platinum(0) Complexes Prepared by Thermal Decomposition of $L_2Pt^{II}R_2$

complex	dec temp, °C (*t*, h)	yield, %	$\delta(^{31}P)$	$J_{Pt,P}$, Hz
$(Et_3P)_2Pt(ethylene)^a$	118 (0.5)	100^c	20.6	3551
$(Me_3P)_2Pt(ethylene)^b$	118 (1.2)	$>70^d$	$-19.5^{e,f}$	$3435^{e,f}$
$(Et_3P)_2Pt(propylene)^a$	80 (10.0)	$>80^d$	21.1, 18.5	3767, 3279^g
$(Et_3P)_2Pt(cyclobutene)^a$	40 (4.0)	95^d	20.1	3418
$(Et_3P)_2Pt(cyclopentene)^a$	35 (1.0)	75^c	*e*	*e*
$(Ph_3P)_2Pt(cyclobutene)^b$	35 (0.5)	40^d	34.2	3604
$(DMPE)_2Pt^b$	182 (20.0)	95^d	−8.1	3724

[a] Cyclohexane was the solvent for decompositions. [b] Toluene was the solvent for decompositions. [c] Determined by treatment with methyl iodide. [d] Estimated from NMR peak heights. [e] Rapid exchange of R_3P groups was observed in the ^{31}P NMR spectrum at room temperature. [f] At −45 °C. [g] $J_{P,P} = 66$ Hz.

Dicyclobutylbis(triphenylphosphine)platinum(II). This compound was prepared by a procedure similar to that described for the triethylphosphine complex except as noted. Triphenylphosphine was added to the solution of $(COD)Pt(C_4H_7)_2$ as a solution in a minimum volume of diethyl ether at 0 °C. The product precipitated directly from the ether solution without addition of methanol, giving 0.42 g (41%) of white needles, mp 87–97 °C dec. ^{31}P NMR: $\delta = 26.3$ ($J_{Pt,P} = 1709$ Hz).

Dicyclopentylbis(triethylphosphine)platinum(II). In a 250-mL round-bottomed flask was placed 0.50 g (1.3 mmol) of $(COD)PtCl_2$. The flask was fitted with a stirring bar, sealed with a rubber septum, and flushed thoroughly with argon. Into the flask was transferred 100 mL of ether via cannula, and the mixture was cooled to −50 °C. To the stirred mixture was added by syringe 10.0 mL of 0.60 M cyclopentylmagnesium bromide in THF. The reaction mixture was stirred vigorously at −50 °C for 4 h, warmed slowly to −20 °C, and stirred for an additional 4 h. The reaction was quenched by addition of 10 mL of 20% methanol in water by syringe. The ether layer was decanted via cannula into a 100-mL flask and the ether removed at −20 °C under reduced pressure to a volume of ca. 10 mL. Cold methanol (30 mL) containing 1.00 mL (0.810 g, 6.86 mmol) of triethylphosphine was added to this solution. The solution was stirred for 3 h at −20 °C during which time a white crystalline solid precipitated. The solution was further concentrated at reduced pressure, cooled to −30 °C, and filtered rapidly on a coarse frit. The product was washed with two 3-mL portions of cold (−30 °C) methanol and dried in vacuo to give an off-white solid in 43% overall yield; mp 59–61 °C dec. ^{31}P NMR: $\delta = 9.0$ ($J_{Pt,P} = 1616$ Hz).

General Decomposition Procedure. Thermal decompositions of diethyl- and dipropylplatinum(II) complexes were carried out in sealed tubes by procedures analogous to that described below for the preparation of ethylenebis(triethylphosphine)platinum(0). Indistinguishable results have been obtained in serum-capped tubes under argon.[12] Cyclobutyl and cyclopentyl complexes were decomposed in serum-stopped test tubes under an argon atmosphere. ^{31}P NMR data for all new platinum(0) complexes are in Table I. Yields of platinum(0) complexes were determined either by measuring the yield of iodomethylbis(phosphine)platinum(II) obtained after reaction with methyl iodide or by estimating ^{31}P NMR peak heights relative to triethylphosphate internal standard. Comparable results were obtained by either method.

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[1] Supported by the National Science Foundation, Grant CHE 7711282.

[2] National Institutes of Health Predoctoral Trainee, 1977–1979.

[3] National Science Foundation Predoctoral Fellow, 1978–1981.

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