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be concluded that, in the dinuclear compound, either electrostatic effects or electron delocalization is responsible for the large, 300-mV separation of the ruthenium-based redox couples.

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Synthesis and Deprotonation Reactions of Neutral and Cationic Cyclic (Aminooxy)carbenes Derived from Platinum(II) Carbonyls

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Stable α-heteroatom-substituted (N, O, S) carbene complexes of platinum(II) have been prepared by either nucleophilic or electrophilic addition to a number of metal-coordinated ligands,[1] yet none have been reported from a carbon monoxide group. On the other hand, platinum group carbonyls are susceptible to nucleophilic attack, and their reactions with amines, alcohols, and water yield carbamoyl, alkoxy carbonyl, and hydroxy carbonyl complexes, respectively.[2]

Recent research work by Angelici and co-workers and some of us have been concerned with the reactions of 2-haloethanols, (2-haloethyl)amines, and the three-membered heterocycles $\overline{\mathrm{YCH_2C}}\mathrm{H_2}$ (Y = NH, O) with electrophilic carbonyl[3] and isocyanide[4] ligands to afford cyclic carbene complexes. In order to explore the generality of these reactions also with square-planar platinum(II) carbonyls, we report herein the synthesis and some deprotonation reactions of (aminooxy)carbene complexes derived from CO ligands.

Experimental Section

General Information. Experimental procedures and starting reagents were as previously reported.[4] IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer; ^{31}P NMR spectra were run on a Varian FT 80 A spectrometer. Melting points were determined on a hot-plate apparatus and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. The fast atom bombardment of **7** was obtained on a VG ZAB 2F instrument, operating with a Xe atom beam energy of 8 keV. The molecular weight measurements of **7** were taken on a Knauer osmometer at 36 °C with 1,2-dichloroethane as solvent. The complexes *cis*-$\mathrm{Cl_2(PPh_3)Pt(CO)}$,[5] *cis*-$\mathrm{Cl_2(PMe_2Ph)Pt(CO)}$,[5] *trans*-$\mathrm{[(PPh_3)_2ClPt(CO)]BF_4}$,[2c] *trans*-$\mathrm{[(PPh_3)_2(CF_3)Pt(CO)]PF_6}$,[6] and *trans*-$\mathrm{[(PPh_3)_2HPt(CO)]BF_4}$,[6] were obtained as described in the literature.

Synthesis of *trans*-$\mathrm{[(PPh_3)_2Pt(\overline{COCH_2CH_2N}H)X]BF_4}$ [X = Cl (1a), Br (1b)]. These complexes were prepared by a procedure similar to that described herein for **1a**. To a stirring suspension of $\mathrm{Cl[NH_3CH_2CH_2Cl]}$ (116 mg, 1.00 mmol) in THF (30 mL) at 0 °C was added aziridine (0.050 mL, 1.00 mmol) and then solid *trans*-$\mathrm{[(PPh_3)_2ClPt(CO)]BF_4}$ (870 mg, 1.00 mmol). After 1 min, a solution IR spectrum revealed no ν(CO) absorption at 2121 cm^{-1} of the carbonyl complex. The reaction mixture was stirred at 0 °C for 30 min, and then stirring was continued for 3 h at room temperature to give a pale yellow suspension. The solution was taken to dryness under reduced pressure, and the residue was taken up with $\mathrm{CH_2Cl_2}$ (20 mL). To the filtered solution was added dropwise *n*-hexane (80 mL) to give a white solid, which was filtered, washed with *n*-hexane (2 × 5 mL), and dried under vacuum: yield 685 mg, 75%; mp 242–244 °C dec. Anal. Calcd for $\mathrm{C_{39}H_{35}NClOP_2PtBF_4}$: C, 51.68; H, 3.86; N, 1.53; Cl, 3.88. Found: C, 51.68; H, 3.80; N, 1.50; Cl, 3.92. Compound **1b** (45%) was obtained, together with **1a** (25%) and *cis*-$\mathrm{(PPh_3)_2PtCl(Br)}$ (20%), by reaction of $\mathrm{Br[NH_3CH_2CH_2Br]}$ (104 mg, 0.50 mmol), aziridine (0.024 mL, 0.48 mmol), and *trans*-$\mathrm{[(PPh_3)_2PtCl(CO)]BF_4}$ (400 mg, 0.46 mmol) with the same experimental procedure reported for **1a**. The percentage yields were deduced by integration of the ^{31}P resonances of the product mixture. The complex *cis*-$\mathrm{(PPh_3)_2PtCl(Br)}$ [dd, δ(P(trans to Cl)) 14.74 (d), $^1J_{\mathrm{PPt}} = 3642$ Hz; δ(P(trans to Br)) 12.30 (d), $^1J_{\mathrm{PPt}} = 3660$ Hz; $^2J_{\mathrm{PP}} = 13.8$ Hz] was identified by comparison with the ^{31}P NMR spectrum of a sample obtained on stirring *cis*-$\mathrm{(PPh_3)_2PtCl_2}$ (269 mg, 0.34 mmol) and LiBr (15 mg, 0.17 mmol) in acetone (10 mL) at room temperature for 24 h.

***trans*-$\mathrm{[(PPh_3)_2Pt(\overline{COCH_2CH_2N}H)Br]Br}$ (1c).** A stirring suspension of $\mathrm{Br[NH_3CH_2CH_2Br]}$ (100 mg, 0.49 mmol) in THF (20 mL) at 0 °C was treated with a 1.4 M *n*-hexane solution of *n*-BuLi (0.38 mL, 0.53 mmol). To the colorless solution was added solid *trans*-$\mathrm{[(PPh_3)_2PtCl(CO)]BF_4}$ (200 mg, 0.23 mmol). A solution IR spectrum taken immediately revealed no ν(CO) absorption. The yellow reaction mixture was allowed to reach room temperature. Stirring was then continued for 2 days, during which time a pale yellow solid started to precipitate. Workup as for **1a** afforded 162 mg, 75%; mp 228–231 °C (dec). Anal. Calcd for $\mathrm{C_{39}H_{35}NBr_2OP_2Pt}$: C, 49.28; H, 3.71; N, 1.47; Br, 16.81. Found: C, 48.93; H, 3.59; N, 1.43; Br, 16.40.

Similarly, compound **1a** was isolated by reaction of $\mathrm{Cl[NH_3CH_2CH_2Cl]}$ (74 mg, 0.36 mmol) and *n*-BuLi (1.4 M in *n*-hexane, 0.26 mL, 0.36 mmol) with *trans*-$\mathrm{[(PPh_3)_2ClPt(CO)]BF_4}$ (140 mg, 0.16 mmol) in THF (15 mL) after stirring for 1 day at room temperature: yield 130 mg, 92%.

***trans*-$\mathrm{[(PPh_3)_2Pt(\overline{COCH_2CH_2N}H)(CF_3)]PF_6}$ (2).** A stirring suspension of $\mathrm{Br[NH_3CH_2CH_2Br]}$ (94 mg, 0.56 mmol) in THF (20 mL) at 0 °C was treated with aziridine (0.023 mL, 0.46 mmol), and then to the mixture was added solid *trans*-$\mathrm{[(PPh_3)_2Pt(CF_3)(CO)]PF_6}$ (442 mg, 0.46 mmol). A solution IR spectrum revealed the immediate disappearance of the ν(CO) absorption at 2143 cm^{-1}. Stirring was continued for 24 h.

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Then, the reaction mixture was taken to dryness under reduced pressure, and the residue was taken up with CH_2Cl_2. The filtered solution was taken to dryness. Addition of Et_2O (10 mL) and a few drops of MeOH afforded a white solid that was filtered out and dried under vacuum: yield 90 mg, 30%, mp 240–243 °C dec. Anal. Calcd for $C_{40}H_{35}NF_9OP_3Pt$: C, 47.82; H, 3.51; N, 1.39 Found: C, 47.50; H, 3.42; N, 1.31.

***cis*-$\mathbf{Cl_2Pt(\overline{COCH_2CH_2N}H)(L)}$ [L = $\mathbf{PPh_3}$ (3), $\mathbf{PMe_2Ph}$ (4)].** Complex **3** was obtained by starting with *cis*-$Cl_2(PPh_3)Pt(CO)$ (334 mg, 0.60 mmol), $Cl[NH_3CH_2CH_2Cl]$ (70 mg, 0.60 mmol), and aziridine (0.030 mL, 0.60 mmol) in THF (20 mL) at 0 °C. A solution IR spectrum showed the absence of the ν(CO) absorption at 2105 cm^{-1} after 1 h of reaction at 0 °C. Stirring was continued for an additional 3 h at room temperature. Formation of CO_2 was detected in the IR at 2336 cm^{-1} in THF. Workup as for **1a** yielded 246 mg (41%) of **3**; mp 218–221 °C dec. Anal. Calcd for $C_{21}H_{20}NCl_2OPPt$: C, 42.08; H, 3.36; N, 2.34; Cl, 11.83. Found: C, 41.90; H, 3.34; N, 2.33; Cl, 11.85. Compound **4** was obtained similarly by starting from *cis*-$Cl_2(PMe_2Ph)Pt(CO)$ (302 mg, 0.70 mmol), $Cl[NH_3CH_2CH_2Cl]$ (81 mg, 0.70 mmol), and aziridine (0.035 mL, 0.70 mmol). The IR spectrum of the reaction mixture, revealed the presence of the ν(CO) absorption at 2101 cm^{-1} even after 24 h. Nevertheless, the reaction mixture was worked up as for **1a** to yield 120 mg (37%) of **4**; mp 198–201 °C dec. Anal. Calcd for $C_{11}H_{16}NCl_2OPPt$: C, 27.80; H, 3.39; N, 2.95; Cl, 15.01.

Deprotonation Reactions. Synthesis of *trans*-{$\mathbf{(PPh_3)_2Pt[\overline{COCH_2CH_2N}(CH_2CH{=}CH_2)]X}$}$\mathbf{BF_4}$ [X = Cl, Br] (5). A suspension of **1a** (301 mg, 0.33 mmol) in THF (20 mL) at 0 °C was treated with 1.6 M *n*-BuLi in *n*-hexane (0.23 mL, 0.36 mmol). To the pale yellow solution was added an excess of allyl bromide (0.10 mL, 1.18 mmol). The reaction mixture was stirred for 30 min at 0 °C and then allowed to reach room temperature. After 5 h the clear solution was taken to dryness, and the residue was extracted with CH_2Cl_2 (10 mL). Addition of Et_2O (50 mL) to the filtered solution gave a white precipitate of the product: yield 185 mg, 57%; mp 172–175 °C dec. Anal. Calcd for $C_{42}H_{39}NBrOP_2PtBF_4$: C, 50.57; H, 3.94; N, 1.40. Found: C, 50.19; H, 3.88; N, 1.32.

{$\mathbf{(PPh_3)_2Pt[\overline{COCH_2CH_2N}(CH_2C{\equiv}CH)]X}$}$\mathbf{BF_4}$ [X = Cl, Br] (6). The procedure is identical with that described for the synthesis of **5**: yield 52%; mp 169–172 °C dec. Anal. Calcd for $C_{42}H_{37}NBrOP_2PtBF_4$: C, 50.67; H, 3.75; N, 1.41. Found: C, 50.25; H, 3.60; N, 1.33.

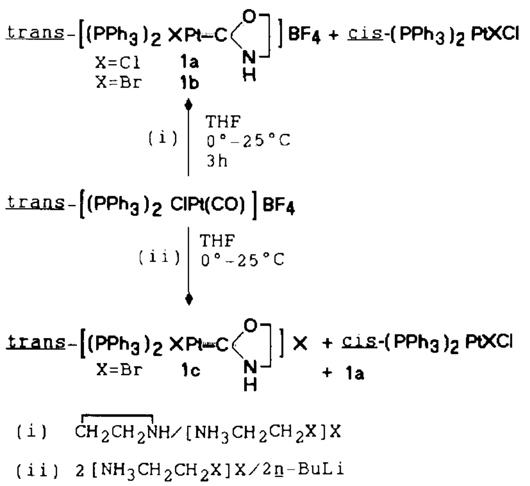
{$\mathbf{(PPh_3)_2ClPt[\mu\text{-}\overline{COCH_2CH_2N}\text{-}}$*C,N*]}$\mathbf{_2}$ (7). To a stirring suspension of **1a** (390 mg, 0.65 mmol) in THF (20 mL) at 0 °C was added in one portion 1.6 M *n*-BuLi in *n*-hexane (0.45 mL, 0.72 mmol). The clear solution was warmed to room temperature and stirred for 20 h, during which time a brownish precipitate formed. The solution was taken to dryness and the residue was extracted with CH_2Cl_2 (30 mL). After filtration, the solution was concentrated to ca. 5 mL under reduced pressure and treated with Et_2O (20 mL) to give an off-white precipitate of the complex: yield 270 mg, 74%; mp >300 °C (ca. 270 °C dec). FAB-MS [*m/z* (relative abundance %)]: $[M + 2H]^+$, 1126 (0.754); $[M + 2H - Cl]^{\bullet+}$, 1091 (1.11), $[M + 2H - 2PPh_3]^+$, 602 (0.75). The average molecular weight measurements gave 1100. Anal. Calcd for $C_{42}H_{38}N_2Cl_2O_2P_2Pt_2$: C, 44.81; H, 3.40; N, 2.49; Cl, 6.30. Found: C, 44.24; H, 3.38; N, 2.44; Cl, 6.60.

Reaction of 7 with HCl. To a stirring mixture of CH_2Cl_2 (10 mL) and MeOH (10 mL) was added acetyl chloride (0.016 mL, 0.22 mmol) and subsequently solid **7** (101 mg, 0.18 mmol) in one portion. The reaction mixture was stirred at room temperature for 2 days. The off-white precipitate formed was filtered off, washed with Et_2O (3 × 10 mL), and dried under vacuum: yield 90 mg, 84%. The product was analytically and spectroscopically identified as **3**.

Results and Discussion

Synthesis and Characterization. Scheme I reports the reactions of the cationic carbonyl complex *trans*-$[(PPh_3)_2ClPt(CO)]BF_4$ with (i) aziridine/$X[NH_3CH_2CH_2X]$ (X = Cl, Br) and (ii) $X[NH_3CH_2CH_2X]$/*n*-BuLi (X = Cl, Br) to yield the corresponding five-membered cyclic (aminooxy)carbene derivatives.

Scheme I



As for route i, there appears to be no difference in the reaction times and yields of the carbene products when the halide salts are changed, as indicated by the immediate disappearance of the $\nu(C{\equiv}O)$ absorption in the IR spectra. When X = Cl, the carbene complex **1a** was recovered in 75% yield after a few hours of reaction, together with a small amount of *cis*-$(PPh_3)_2PtCl_2$, which has been identified by comparison with the ^{31}P NMR spectrum of an authentic sample. When X = Br, the (aminooxy)carbene was obtained at the same time as a mixture of chloro (**1a**) and bromo (**1b**) derivatives in ca. 25% and 45% yields, respectively. Also for this latter reaction, carbonyl substitution by halide produces *cis*-$(PPh_3)_2PtCl(Br)$ (see Experimental Section) in ca. 20% yield, as deduced by integration of the ^{31}P resonances of the reaction products. Compounds **1a**, **1b**, and the dihalo derivatives could not be separated by repeated crystallizations.

Also for route ii, the carbonyl stretching immediately disappears upon reaction with (2-haloethyl)amine, but the carbene products take a longer time to precipitate compared to those found for route i. The formation of small amounts (<5%) of *cis*-$(PPh_3)_2PtCl(X)$ (X = Cl, Br) is observed also in these reactions. Furthermore, complete replacement of the chloride and tetrafluoroborate ions by bromide occurs under prolonged stirring in the cyclization reaction leading to **1c**. A similar behavior was observed in the reaction of *trans*-$[L_2Pt(CNR)Cl]BF_4$ complexes with excess $Br[NH_3CH_2CH_2Br]$ and *n*-BuLi.[4b]

We have examined also the reaction of *trans*-$[(PPh_3)_2ClPt(CO)]BF_4$ with aziridine alone. Addition of 1 equiv of aziridine in THF at 0 °C leads to the immediate disappearance of the $\nu(C{\equiv}O)$ band at 2121 cm^{-1}, with no carbamoyl absorption being detected. From this reaction, complex **1a** was formed (ca. 70% yield) together with other impurities, which could not be identified and separated from **1a**. This reaction takes a longer time to complete (ca. 24 h) in comparison with those carried out in the presence of a halide ion.

It has been reported that the CO ligand reactivity toward nucleophilic attack in cationic complexes *trans*-$[(PPh_3)_2XPt(CO)]^+$ depends markedly on the σ-donor ability of the trans ligand X (X = anionic ligand).[2b] As for *trans*-$[(PPh_3)_2RPt(CO)]^+$ (R = CF_3, H), the reactions with aziridine/halide ion systems are reported in Scheme II. The results indicate that the Pt(II)–CO → Pt(II)–carbene conversion decreases with increasing σ-donor ability of the trans ligand X, and when X = H, the CO substitution process is the only occurring reaction.

The reaction of *trans*-$[(PPh_3)_2ClPt(CO)]^+$ with $BrCH_2CH_2OH$ alone proceeds rapidly at room temperature to give quantitatively *cis*-$(PPh_3)_2PtBr_2$, with no bromo alkoxy carbonyl intermediate being observed by monitoring the reaction course by IR spectroscopy. The formation of the dibromo derivative may be explained by displacement of the carbonyl ligand with bromide ion due to the presence of HBr in the reacting 2-bromoethanol. The reaction of *trans*-$[(PPh_3)_2ClPt(CO)]^+$ with $XCH_2CH_2O^-$, even at low temperature, always leads to the formation of a mixture of *trans*-$(PPh_3)_2PtH(X)$[7] and *cis*-$(PPh_3)_2PtX_2$ derivatives. Presumably the hydrido derivative may originate by nucleophilic

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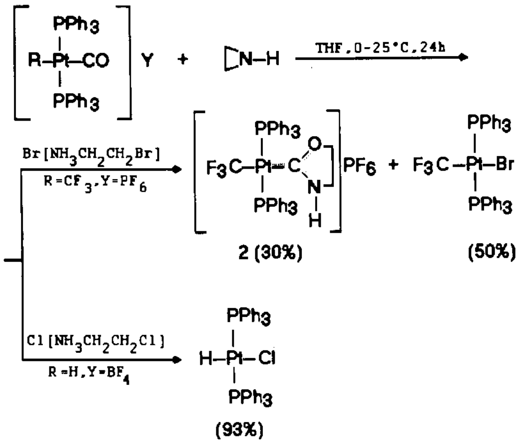
Table I. IR and ^{1}H and ^{31}P NMR Data for Cyclic (Aminoxy)carbene Complexes of Pt(II)

	IR^a			^{1}H NMR^b				^{31}P{^{1}H} NMR^c	
compd	ν(CN)	ν(NH)	ν(PtCl)	$\delta(OCH_2)$	$\delta(NCH_2)$	$^3J_{HH}$	δ(other)	δ(P)	$^1J_{PPt}$
1a	1564 m	3274 w	319 m	3.38 t	2.45 t	9.6	9.23 s^d	17.71 s	2532
1b	1563 m	3260 w		3.38 t	2.44 t	9.2	9.59 br^d	15.97 s	2509
1c	1561 m	*e*		3.38 t	2.38 t	9.6	*e*	15.81 s	2542
2	1563 s	3374 s		3.34 t	2.32 t	9.6	8.29 br^d	16.06 q^f	2762
3	1552 s	3217 s	317 m, 281 m	3.97 t	3.27 t	9.8	9.30 br^d	7.89 s^g	3957
4	1549 s	3319 s	293 m, 314 m	4.14 t	3.42 t	9.3	9.59 s,^{d} 1.99 d^h	−14.14 s	3763
5^i	1549 m			3.68 t	2.76 t	9.7	4.03 d,^{j} 5.29 m^k 5.21 m^l	16.26 s^m 18.14 s^n	2474 2501
6^o	1542 m			3.61 t	2.87 t	9.6	2.49 t,^{p} 4.28 d^q	15.97 s^m 17.78 s^n	2444 2470
7	1542 s		290 m	3.87 m^r	3.26 q,^{r} 2.75 m^r			10.53 s	3698

^{a} Nujol mull; ν in cm^{-1}. Abbreviations: s = strong, m = medium, w = weak. ^{b} Spectra recorded in $CDCl_2$. Proton chemical shifts are referenced to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. J in Hz. ^{c} Phosphorous chemical shifts are from external H_3PO_4, 85%; positive chemical shifts are downfield from the reference. Abbreviations: s = singlet, q = quartet. ^{d} δ(NH). ^{e} NH signal not located. ^{f} $^3J_{PF}$ = 15.7 Hz. ^{g} In DMSO-d_6. ^{h} P–Me. ^{i} ν(C=C) not detected. ^{j} $NCH_2CH{=}CH_2$; X = Br, $^3J_{HH}$ = 4.4; X = Cl, 3.99 $^3J_{HH}$ = 5.7. ^{k} $CH{=}CH_2$. ^{l} $CH{=}CH_2$. ^{m} X = Br. ^{n} X = Cl. ^{o} ν(≡CH) 3269 w; ν(C≡C) 2131 w. ^{p} $NCH_2C{\equiv}CH$, X = Br, $^4J_{HH}$ = 2.6. X = Cl, 2.47 t, $^4J_{HH}$ = 2.6. ^{q} $NCH_2C{\equiv}CH$, $^4J_{HH}$ = 2.6, X = Br; X = Cl, 4.23 d, $^4J_{HH}$ = 2.6. ^{r} The system is AA′BC type, where A and A′ are the OCH_2 protons and B and C the NCH_2 protons.

Scheme II



Scheme III

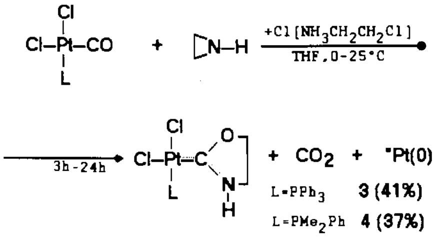


Table II. Selected ^{13}C{^{1}H} NMR^a Spectral Data for the Complexes

compd	$\delta(C)_{carbene}$	$\delta(OCH_2)$	$\delta(NCH_2)$	δ(other)
1c	188.45 t $^2J_{PC}$ = 7.6 $^1J_{CPt}$ = 1363	70.13 s $^3J_{CPt}$ = 35.8	42.95 s $^3J_{CPt}$ = 34.8	
2	207.70 m^b	70.29 s $^3J_{CPt}$ = 35.6	43.01 s $^3J_{CPt}$ = 26.7	
4	183.40 d^b $^2J_{CP}$ = 8.1	71.16 s $^3J_{CPt}$ = 33.1	44.19 s $^3J_{CPt}$ = 43.2	14.10 d^c $^1J_{CP}$ = 44.5
5	190.04 t $^2J_{CP}$ = 7.6 $^1J_{CPt}$ = 1389	72.16 s $^3J_{CPt}$ = 62.3	47.41 s $^3J_{CPt}$ = 88.6	122.92 s^d
7	171.11 dd^b $^2J_{CP}$ = 8.9 $^3J_{CP}$ = 2.5	67.32 s $^3J_{CPt}$ = 50.9	50.84 s $^3J_{CPt}$ = 53.4	

^{a} Spectra recorded in CD_2Cl_2; chemical shifts are referenced to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +53.80 ppm; J in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet. ^{b} ^{195}Pt satellites insufficiently intense to be observed. ^{c} P–CH_3. ^{d} $={CH_2}$; $NCH_2CH{=}$ and $NCH_2CH{=}$ resonances probably masked by phenyl signals.

attack of $XCH_2CH_2O^-$ on the metal to give a Pt(II)–alkoxide intermediate, which then rearranges to the final hydrido species by β-hydrogen abstraction.[8] It is also possible that the reaction of the hydrido derivative with HX may ultimately lead to the formation of *cis*-$(PPh_3)_2PtX_2$.[9]

The reactions of the neutral carbonyl complexes *cis*-$Cl_2Pt(L)(CO)$ (L = PPh_3, PMe_2Ph) with aziridine/Cl^- lead to the formation of neutral cyclic five-membered (aminooxy)carbenes, as reported in Scheme III. The low yields of the carbene products are due to a concomitant nucleophilic attack by water on the carbonyl group to give an unstable Pt–COOH intermediate that subsequently decomposes to produce CO_2 and unidentified species, showing in the IR spectrum a broad band at ca. 1800 cm^{-1} (Nujol). This latter compound can be attributed to a mixed carbonyl–phosphine platinum cluster.[10] The hydrolysis of cationic Pt(II) carbonyls to give hydroxy carbonyl derivatives and their subsequent rearrangement to Pt–H and CO_2 species has been documented.[2e,f]

As described for cationic platinum carbonyls, also the reactions of neutral platinum carbonyls with 2-halo alcohols either alone or in the presence of a base fail to give any dioxycarbene derivative.

Complexes **1**–**4** are stable in the solid state and in solution. They have been characterized by their elemental analyses (Experimental Section) and IR, ^{1}H NMR, and ^{31}P NMR (Table I) spectroscopies. The ^{13}C NMR data for **1c**, **2**, and **4** are reported in Table II. IR and NMR data are comparable to those found for related (aminooxy)carbene derivatives.[3,4]

Within the different synthetic methods investigated, the use of the aziridine/Cl^- system or the $Cl[NH_3CH_2CH_2Cl]$/*n*-BuLi system appears to be more convenient since they avoid undesired metal–halide exchange with formation of a mixture of halo derivatives. Furthermore, the reaction times and yields are not significantly affected on changing the X^- ion.

It is observed that the conversion of the CO ligand to carbene is not a straightforward process but is always accompanied by two main side reactions that are related to the nature of the metal carbonyl complex and that of coordinated ligands. Thus, for cationic carbonyl complexes the greater the σ-donor ability of the ligand trans to the carbonyl (i.e. H > CF_3 > Cl), the more the CO ligand-substitution process is favored (Schemes I and II). Conversely, for neutral Pt(II) carbonyls the nucleophilic attack by water on the CO ligand is the more important side reaction (Scheme III).

It is also apparent that for neutral Pt(II) carbonyls the nucleophilic attack on the carbonyl carbon to give carbenes is in-

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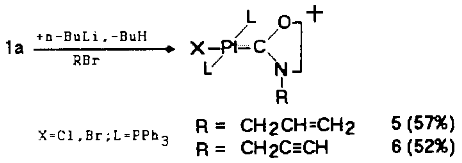
Scheme IV

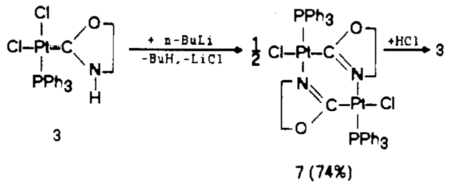


fluenced by electronic effects of the ancillary phosphine ligand L. Thus, when L = PPh_3, the $\nu(C{\equiv}O)$ absorption disappears after 1 h of reaction and gives after 3 h a 41% yield of the isolated product **3**. On the other hand, with the more basic PMe_2Ph ligand the $\nu(C{\equiv}O)$ absorption is still present after 24 h of reaction and gives after the same time a 35% yield of **4**. A similar trend in reactivity has been reported for the reactions of a series of isocyanide complexes of the type *cis*-$Cl_2Pd(CNR)(L)$ (L = phosphite or tertiary phosphine ligand) with amines.[11]

Although carbamoyl intermediates have been proposed to be formed by attack of aziridine/X^- or (haloethyl)amine on several transition-metal carbonyls,[3] we found no IR evidence for such species in the reactions leading to carbene formation. On the other hand, it is worthwhile noting that a recent report of the reaction of a cationic carbonyl complex of Pd(II) with a secondary amine provides direct NMR evidence of the intermediacy of an unstable hydroxyaminocarbene complex,[12] which eventually rearranges to a stable carbamoyl complex.

Deprotonation Reactions. It has been reported that the (aminooxy)-[3a,13] and diaminocarbene[4b] ligands are deprotonated by bases to give imino derivatives whose nitrogen reacts with electrophiles to regenerate carbene complexes. Also the (aminooxy)carbene ligand in **1a** (Scheme IV) is readily deprotonated by *n*-BuLi and subsequently alkylated by allyl bromide and propargyl bromide to give the corresponding *N*-allyl and *N*-propargyl derivatives **5** and **6**, respectively. These complexes are isolated as a mixture of chloro and bromo derivatives, which are formed by metal–halide exchange due to the presence of Br^- ions in the reaction mixtures. Spectroscopic data are in agreement with those reported for similar complexes[4b] and suggest that also for **5** and **6** there is no unequivocal evidence for allyl and propargyl group coordination to Pt(II) in solution. On the other hand, recently an X-ray structure of the Pd(II) complex *trans*-$Cl_2Pd[CN(CH_2CH{=}CH_2)CH_2CH_2N(CH_2CH{=}CH_2)]_2$ containing *N*-allyl diaminocarbene ligands shows that the allyl substituents at nitrogen are not implicated in bonding to palladium, in contrast to the situation found for a related Mo(0) complex *cis*-$(CO)_4Mo[CN(CH_2CH{=}CH_2)CH_2CH_2N(CH_2CH{=}CH_2)]$.[14]

Similar deprotonation reactions with the neutral (aminooxy)carbene **3** lead to the formation of the dimer **7**. No N-alkylation



occurs when the reaction is carried out in the presence of allyl bromide or propargyl bromide, complex **7** being the only isolated product. It is also observed that **7** regenerates **3** upon reaction with HCl.

Compound **7** was characterized by elemental analysis, molecular weight measurements, FAB mass spectrum, and spectroscopic data. The IR spectrum shows no $\nu(N{-}H)$ absorption, while $\nu(C{=}N)$ and $\nu(Pt{-}Cl)$ stretchings are found at 1542 and 290 cm^{-1}, respectively. The ^{31}P NMR spectrum displays one single resonance at δ 10.53 with $^1J_{PPt}$ = 3698 Hz. The ^1H NMR spectrum displays an AA'BC system in the range δ 3.98–2.72. The *cis*-C–Pt–PPh_3 arrangement has been deduced by ^{13}C NMR data. The C–Pt carbon appears as a doublet of doublets at 171.11 with $^2J_{PC}$ = 8.9 Hz and $^3J_{CP}$ = 2.5 Hz.

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