and preparation and study of complexes with the Costa model containing $CH_2C(CH_3)(CO_2C_2H_5)_2$ may elucidate the relative importance of steric and electronic contributions to instability. It is also possible that, during the catalysis, the organic intermediates do not form a direct Co to C bond.[1] Alternatively, a bond between Co and a secondary or tertiary carbon in the alkyl could provide the strain necessary to drive a carbon skeleton rearrangement. Increased strain was observed, as discussed above, in going from $PPh_3(DH)_2(i\text{-}C_3H_7)$ to $PPh_3Co(DH)_2(2\text{-}C_4H_9)$.

The $CH_2C(CH_3)(CO_2C_2H_5)_2$ ligand[29,52] is interesting in that it is a bulky alkyl with electron-withholding substituents. The structural consequences of this have been mentioned above. The Co–P bond length in **3** is anomalously long and may reflect the steric bulk of the alkyl. Steric interactions may be made more serious by the relatively large value of $\sum C\hat{P}C$ for this alkyl. Complexes with bulky alkyl groups bearing electron-withdrawing substituents appear worthy of further study.[53]

Acknowledgment. L.G.M. thanks the Alexander von Humboldt Foundation for a Senior U.S. Scientist Award which facilitated the preparation of this manuscript. This research was supported by NIH Grant GM29225 (LGM) and by a grant to L.R. from CNR, Rome, Italy. We are grateful for this support.

Registry No. 1, 38141-58-1; 2, 94202-45-6; 3, 94202-46-7; 4, 57620-61-8; $PPh_3Co(DH)_2Cl$, 23295-34-3; $PPh_3Co(DH)_2Br$, 33988-32-8; $PPh_3Co(DH)_2I$, 33988-34-0; $PPh_3Co(DH)_2NO_2$, 39038-45-2; $PPh_3Co(DH)_2CH_2CN$, 84662-76-0; $PPh_3Co(DH)_2CH(CH_3)CN$, 94292-13-4; $PPh_3Co(DH)_2CH_2CF_3$, 17567-52-1; $PPh_3Co(DH)_2CH_2Br$, 84662-75-9; $PPh_3Co(DH)_2CH_3$, 15977-37-4; $PPh_3Co(DH)_2(i\text{-}C_3H_7)$, 60293-65-4; $PPh_3Co(DH)_2(\text{neo-}C_5H_{11})$, 82405-10-5; PBu_3, 998-40-3; $BrCH_2C(CH_3)(CO_2C_2H_5)_2$, 75511-41-0; CH_2Br_2, 74-95-3; diethyl methylmalonate, 609-08-5.

Supplementary Material Available: A listing of structure factors and tables of anisotropic thermal parameters and hydrogen atom parameters (74 pages). Ordering information is given on any current masthead page.

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[52] Grate, J. H.; Grate, J. W.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1982,** *104,* 1588.

[53] A reviewer has suggested that the ^{31}P NMR can be correlated by a two-parameter fit with Co–P bond distance and $\sum CPC$. We are examining this issue.

Aryldiazenido (N_2Ar) Complexes. Carboxylate, Formate, Hydroxycarbonyl, and Hydride Derivatives of $[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)][BF_4]$ and $[(\eta\text{-}C_5Me_5)Re(CO)_2(N_2Ar)][BF_4]$

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The aryldiazenido complexes $[(\eta\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4R)][BF_4]$ (**1**: **a**, R = Me; **b**, R = OMe; **c**, R = NEt_2) and $[(\eta\text{-}C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4R)][BF_4]$ (**7**, R = OMe) react with a stoichiometric amount of 0.1 M aqueous NaOH to give the air-stable, microcrystalline, golden yellow hydroxycarbonyl complexes $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (**2**) and $(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (**8**). These complexes dissolve in excess aqueous hydroxide to give bright yellow solutions of the respective carboxylate complex anions $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-$ (**4**) and $[(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-$ (**10**), which have been isolated as lithium or calcium salts. Under specified conditions, which are discussed, decarboxylation occurs to yield the yellow hydride complexes $(\eta\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4R)$ (**3**) and $(\eta\text{-}C_5Me_5)ReH(CO)(p\text{-}N_2C_6H_4R)$ (**9**). Formate complexes $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(OCHO)$ (**5**) and $(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4R)(OCHO)$ (**11**), isomeric with the hydroxycarbonyl complexes, have also been synthesized for comparison.

Introduction

Recent work in this laboratory on the characterization and study of complexes containing the aryldiazenido ligand (N_2Ar; Ar = aryl) has centered on the cationic dicarbonylcyclopentadienylrhenium derivatives $[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)]^+$ (**1**).[1] These compounds have been particularly interesting to us because, in contrast with most aryldiazenido complexes, the N_2Ar ligand reacts readily with various nucleophiles and thereby can be transformed, for example, to a dinitrogen ligand[1] (eq 1) or to substituted diazene or hydrazide ligands[2] (eq 2).

$$1 + NaI \rightarrow (\eta\text{-}C_5H_5)Re(CO)_2(N_2) \qquad (1)$$

$$1 + CH_3Li \rightarrow (\eta\text{-}C_5H_5)Re(CO)_2[NN(CH_3)Ar] \qquad (2)$$

Although there is a well-known formal analogy between nitrosyl (NO) and organodiazenido ligands, it is notable that in reactions of the corresponding rhenium nitrosyl cation $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ with nucleophiles, it never appears that the nitrosyl ligand is transformed. Instead, this nitrosyl complex and the triphenylphosphine analogue

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[1] Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980,** *19,* 2740.

[2] Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982,** *21,* 2578.

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$[(\eta\text{-}C_5H_5)Re(CO)(PPh_3)(NO)]^+$ are remarkable for their ability to react with nucleophiles at a carbonyl group and yield products in which the new organic functional groups thus formed are stabilized. One example is the transformation of a CO group to HCO, CH_2OH, and CH_3 ligands by borohydride reductions.[3-7,9] Another is the preparation of the hydroxycarbonyl (or metallocarboxylic acid) complexes $(\eta\text{-}C_5H_5)Re(CO)(NO)(COOH)$[8] and $(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(COOH)$[9] using hydroxide ion.

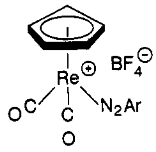
Hydroxycarbonyl complexes have been invoked to account for a number of important processes, including homogeneous catalysis of the water gas shift reaction[10-12] and the formation of hydride ligands by water or hydroxide ion attack on coordinated carbonyl groups.[13,14] Nevertheless, only a very limited number of such complexes has been synthesized, and few have been fully characterized.[15] The most recent and comprehensive characterization of a stable hydroxycarbonyl complex is that reported by Sweet and Graham[8] for $(\eta\text{-}C_5H_5)Re(CO)(NO)(COOH)$.

In this paper we show that stable and well-characterized hydroxycarbonyl complexes of formula $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (2: **a**, R = Me; **b**, R = OMe; **c**, R = NEt_2) can similarly be synthesized by hydroxide ion addition to the aryldiazenido complexes **1**. The isomeric formate complex $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(OCHO)$ (**5**) has also been synthesized for comparison. The chemistry of these hydroxycarbonyl complexes **2**, particularly with reference to the conditions for their conversion to the hydride complexes $(\eta\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4R)$ (**3**) and the anionic carboxylate complexes $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-$ (**4**), is discussed. Finally, the study has been repeated for the pentamethylcyclopentadienyl analogues in order to compare the effect of replacing the $(\eta\text{-}C_5H_5)$ group by $(\eta\text{-}C_5Me_5)$ on the properties of these compounds. A preliminary account of some of this work has been published.[16]

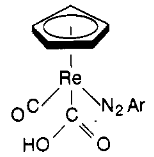
Results and Discussion

The products obtained in the reactions of alkali-metal hydroxides with the cyclopentadienyl complexes $[(\eta\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4R)][BF_4]$ (**1**) are exceedingly dependent on the reaction conditions, the solvents, the alkali metal, and whether excess hydroxide is present. It is possible to obtain the hydroxycarbonyls $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (**2**), the hydrides $(\eta\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4R)$ (**3**), the anionic carboxylate complexes $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-$ (**4**), and the dinitrogen complex $(\eta\text{-}C_5H_5)Re(CO)_2(N_2)$.

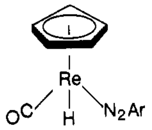
In preliminary studies, solutions of compounds **1** in CH_2Cl_2 at room temperature reacted rapidly with excess aqueous 5 M NaOH, and the hydrides **3** plus a large amount of the dinitrogen complex were isolated from the organic phase. A similar reaction for **1c**, conducted under phase-transfer conditions using Et_4NBr as the phase-transfer catalyst, gave comparable results, though less dinitrogen complex seemed to be formed. When reactions were carried out by stirring solid KOH or NaOH pellets with a CH_2Cl_2 solution of **1b**, IR monitoring showed ν(CO) at 2078 and 2020 cm^{-1} from **1b** plus absorption at 1952 cm^{-1} from a transient monocarbonyl complex, which decayed with formation of ν(CO) at 1925 cm^{-1} characteristic of the hydride **3b**. Simultaneously, steadily increasing ν(NN) and ν(CO) absorptions of the dinitrogen complex were observed suggesting it to be formed by a competing reaction. The transient monocarbonyl species was considered probably to be the hydroxycarbonyl complex **2b**, and so further work was directed toward the isolation and characterization of this and the hydride complex. With these in hand, the proposed intermediacy of the hydroxycarbonyl in the synthesis of the hydride could be evaluated in proper detail.



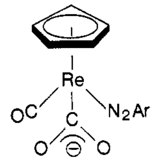
1 (C_5H_5)
7 (C_5Me_5)



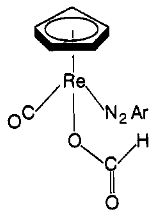
2 (C_5H_5)
8 (C_5Me_5)



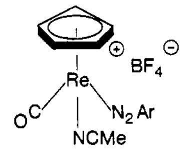
3 (C_5H_5)
9 (C_5Me_5)



4 (C_5H_5)
10 (C_5Me_5)



5 (C_5H_5)
11 (C_5Me_5)



6 (C_5H_5)
12 (C_5Me_5)

Hydroxycarbonyl Complexes $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (2) and $(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(COOH)$ (8). Hydroxycarbonyl complexes **2a–c** and **8** were obtained as analytically pure golden yellow microcrystalline precipitates by the careful, slow addition of a stoichiometric amount of 0.1 M aqueous NaOH to suspensions of **1a–c** or **7** in water (in which they are partly soluble to give reddish (**1a**, **1b**, or **7**) or green (**1c**) solutions). These complexes are stable in air. They are thermally stable as solids up to about 90 °C whereupon they decompose without melting. All are insoluble in water when pure and free from traces of base and display amphoteric behavior since they dissolve in dilute mineral acid to regenerate the parent dicarbonyl cations **1a–c** or **7** and dissolve in excess aqueous hydroxide to give bright yellow solutions considered to contain the anionic carboxylate

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(3) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741.

(4) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (b) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1979**, *173*, C9.

(5) Tam, W.; Wong, W. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

(6) Wong, W. K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.

(7) Wong, W. K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440.

(8) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982.

(9) Tam, W.; Lin, G. Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(10) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3969.

(11) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(12) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

(13) Kruck, T.; Noack, M. *Chem. Ber.* **1964**, *97*, 1693.

(14) Clark, H. C.; Jacobs, W. J. *Inorg. Chem.* **1970**, *9*, 1229.

(15) See ref 8 and references therein.

(16) Barrientos-Penna, C. F.; Gilchrist, A. B.; Sutton, D. *Organometallics* **1983**, *2*, 1265.

complexes 4 or 10 (see below). The latter, when treated with acid, regenerate first the hydroxycarbonyls and then the parent cations (eq 3).

$$\underset{1}{[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)]^+} \xrightleftharpoons[H^+]{OH^-} \underset{2}{(\eta\text{-}C_5H_5)Re(CO)(N_2Ar)(COOH)} \xrightleftharpoons[H^+]{OH^-} \underset{4}{[(\eta\text{-}C_5H_5)Re(CO)(N_2Ar)(CO_2)]^-} \quad (3)$$

The hydroxycarbonyls have been fully characterized by analysis, IR, and ^{1}H NMR. All **2a–c** exhibit in the IR spectrum in CH_2Cl_2 a strong terminal ν(CO) band at about 1950 cm^{-1} and two or three strong and broad bands in the region 1660–1550 cm^{-1} which correspond to the ν(CO) stretching and δ(COH) bending modes of the COOH group and to ν(NN). In **8** ν(CO) is, as expected, at somewhat lower wavenumber (1933 cm^{-1} in CH_2Cl_2) resulting from the more electron-releasing η-C_5Me_5 ligand. This effect is a generally observed one for all of the related (η-C_5H_5) and (η-C_5Me_5) compounds in this study. Attempts to identify unambiguously a particular band corresponding to ν(NN) failed, since several bands shifted under ^{15}N-isotopic substitution at N^1 in the complex **2a**, confirming that ν(NN) is strongly coupled to other vibrational modes in this region. The aryldiazenide group in the parent cations is singly bent (ν(NN) ca. 1770 cm^{-1} for **2a–c** and 1736 cm^{-1} for **7**), and a ν(NN) value of ca. 1600 cm^{-1} is a reasonable one for the singly bent ligand in a neutral complex. On this and electron-counting arguments, these hydroxycarbonyls (and indeed all other the aryldiazenide derivatives in this study) undoubtedly retain the aryldiazenide ligand in the singly bent form.

In the ^{1}H NMR, all **2a–c** and **8** show a broad band at δ 8–9, which integrates as 1 H and is assigned to the carboxylic proton. These values agree well with those reported for other hydroxycarbonyl complexes (η-C_5H_5)Re(CO)(NO)(COOH)[8] (9.5), PtCl$(PEt_3)_2$(COOH)[17] (8.5), and (η-C_5H_5)Re(NO)(PPh_3)(COOH) (10.45–8.86, −80 °C to −30 °C, CD_2Cl_2).[9,18]

Electron-impact mass spectral analysis did not give the molecular peak for the hydroxycarbonyl complexes **2** or **8**, even when a low electron voltage (12 eV) and lower temperatures (ion source = 40 °C) were used. Instead, the parent peak of the hydride complex was obtained. Evident decomposition of the hydroxycarbonyl **2a** to the hydride **3a** during the run was demonstrated by noting that very similar time profiles were obtained for the total ion current (i.e., the production of volatiles from the sample) and the ion currents for *m/e* 44 (CO_2) and 400 [(η-C_5H_5)^{187}ReH(CO)(p-$N_2C_6H_4Me$)].[19] Corresponding results were obtained for **8**. Using fast atom bombardment (FAB), however, the (M + H)$^+$ peak for **2b** was clearly observed and was accompanied by the (M − OH)$^+$ peak (i.e., the cation **1a**) which was some 10 times more intensive. In the case of **8**, the FAB spectrum was dominated by the (M − OH)$^+$ peak, and the (M + H)$^+$ one was not observable above background. For both compounds **2b** and **8**, the spectra provided little, if any, unambiguous evidence of formation of the hydride under fast atom bombardment conditions.

Despite the strong probability, on the basis of the foregoing evidence (and the method of synthesis), that compounds **2a–c** and **8** are indeed hydroxycarbonyl complexes, we considered it important to demonstrate that we were not in fact dealing with the isomeric formate complexes. Though we did not think it likely, the possibility did exist that the hydroxide addition step might be followed by a rearrangement of the COOH group to OCHO (though it is difficult to believe that the OCHO ligand would exhibit the observed amphoteric behavior). Furthermore, the ^{1}H NMR resonance of the proton might (and indeed does) occur at low field in both and could be confused. The authentic formate complexes (η-C_5H_5)Re(CO)(p-$N_2C_6H_4OMe$)(OCHO) (**5**) and (η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(OCHO) (**11**) were synthesized from sodium formate and the cationic acetonitrile complexes [(η-C_5H_5)Re(CO)(CH_3CN)(p-$N_2C_6H_4OMe$)][BF_4] (**6**) and [(η-C_5Me_5)Re(CO)(CH_3CN)(p-$N_2C_6H_4OMe$)][BF_4] (**12**). These are stable in solution in diethyl ether, $CHCl_3$, or acetone at room temperature, and the formate protons occur slightly upfield compared with the hydroxycarbonyl ones: at δ 7.70 in $CDCl_3$ for **5** (cf. δ 8.4 for **2b**) and at δ 7.81 for **11** in acetone-d_6 (cf. δ 9.41 for **8**). The electron-impact mass spectrum of **5** exhibited M$^+$ and (M − CO)$^+$ in a ratio of ca. 1:4 but no fragments corresponding to (M − CO_2)$^+$ or (M − CO − CO_2)$^+$ could be observed above background. Similarly, no production of the (M − CO_2)$^+$ mass, nor that of CO_2, was evident from a trace of their corresponding ion currents during the run. The mass spectrum of the (η-C_5Me_5) compound **11** under similar conditions exhibited M$^+$, M − CO$^+$, *and* M − CO_2^+ in ratios 1:5:3, and production of CO_2 was evident from the mass 44 ion current. We conclude that decarboxylation of the formate group in these complexes is made more favorable by replacing (η-C_5H_5) by (η-C_5Me_5) and that the decarboxylation mechanism for these and the related nitrosyl analogues is worthy of further study in view of the recent interest in this topic.[20]

Carboxylate Complexes [(η-C_5H_5)Re(CO)(p-$N_2C_6H_4R$)(CO_2)]$^-$ (4) and [(η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(CO_2)]$^-$ (10). It has already been pointed out elsewhere in this paper that the hydroxycarbonyls **2a–c** and **8** are soluble in excess aqueous hydroxide to form bright yellow solutions that are considered to contain the carboxylate complexes **4** or **10** (eq 3). Corresponding metallocarboxylate anions have been suggested to be formed in similar reactions of the hydroxycarbonyls (η-C_5H_5)Re(CO)(NO)(COOH)[4] and (η-C_5H_5)Fe(PPh_3)(CO)(COOH)[21] with excess aqueous hydroxide. Only in the latter case was the anion isolated, but then no details of its characterization or properties were given. Noting the previous lack of detailed information on this rare and interesting class of compound, we have fully characterized the ones found here.

Considering first the cyclopentadienyl, the presence of the carboxylate anion **4** in basic solution is suggested by

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[17] Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566.

[18] D. Senn and J. A. Gladysz, personal communication of unpublished data. An earlier report[9] of δ 1.62 ($CDCl_3$) for the COOH proton in this compound was in error.

[19] However, when heated in a sealed tube, the solid hydroxycarbonyl **3b** decomposed at about 85 °C to give a gummy, dark material which IR (CH_2Cl_2) showed *not* to contain the hydride complex. Absorptions from (η-C_5H_5)Re$(CO)_3$ and (η-C_5H_5)Re$(CO)_2(N_2)$ were observed, as in the solution decomposition results described in the text.

[20] Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782. We also note, in passing, significant differences in the FAB mass spectra for **5** and **11**. The FAB spectrum of **11** (xenon–sulfolane) exhibited strong ^{187}Re signals at *m/e* 513 (M − OH$^+$), i.e., the dicarbonyl cation **7**, 502 (M − CO$^+$) and 485 (M − HCO_2^+) and/or (M − OH − CO$^+$) and 429 (M − N_2 − CO − HCO_2^+); the (M + H$^+$) peak at *m/e* 531 occurred weakly and peaks for M$^+$ or (M − CO_2^+) were unobservable above background. Although the cation **7** is very stable and is commonly observed as an intense FAB fragment from the ionization of appropriate neutral parents (e.g., loss of OH$^-$ from the hydroxycarbonyls **2** or **8**), we are surprised to observe it formed from the formate **11**. In contrast, the FAB spectrum of formate **5** does not produce the cation **1b** but gives instead the expected fragments *m/e* 461 (M + H$^+$), 432 (M − CO$^+$), and 415 (M − OCHO$^+$) or (M − OH − CO$^+$).

[21] Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

the following. (i) This reaction is reversed by the addition of aqueous acid which regenerates first the insoluble hydroxycarbonyl **2** and then the parent dicarbonyl cation **1**, in agreement with eq 3. (ii) The ^1H NMR observed when a suspension of **2b** in D_2O was treated with excess NaOD in D_2O indicated the presence of just a single rhenium species with δ 5.82 (η-C_5H_5) and other resonances attributable only to the *p*-$N_2C_6H_4OMe$ protons. Furthermore, this spectrum corresponds exactly with that observed for D_2O solutions of authentic Li and Ca carboxylates subsequently isolated (see below).

When the bright yellow solutions generated by using excess NaOH or KOH and **2b** were pumped at room temperature, a dark yellow, gummy residue was obtained. The rhenium compound present extracted completely into organic solvents, including hexane and CH_2Cl_2, but IR and ^1H NMR showed it now to be the hydride (η-C_5H_5)ReH(CO)(*p*-$N_2C_6H_4OMe$) (**3b**). Note that the hydride is insoluble in water and cannot have been the compound responsible for the original bright yellow basic solutions. Using aqueous LiOH or $Ca(OH)_2$ gave, on evaporation, light yellow solids from which, in each case, CH_2Cl_2 extracted a yellow material which spectroscopically was clarly not the hydride **3b**. Furthermore, this could be precipitated by addition of hexane as an air-stable, light yellow solid and was characterized as the CH_2Cl_2 solvate of the Li or Ca salt of the carboxylate anion $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]^-$ (**4b**).[22] Alternatively, the lithium compound was synthesized in hexane from the hydroxycarbonyl **2b** and CH_3Li.

The lithium salt, for example, exhibits in the IR spectrum in CH_2Cl_2 a strong terminal ν(CO) band at 1944 cm^{-1} (compare 1952 cm^{-1} for the hydroxycarbonyl **2b** and 1925 cm^{-1} for the hydride **3b**) and bands at 1625 and 1580 cm^{-1} assigned to ν(NN) and the carboxylate group. The ^1H NMR spectrum in D_2O is virtually identical with that described above when **2b** was treated with excess NaOD, so the carboxylate is evidently produced in aqueous solution irrespective of the soluble metal hydroxide employed. The ^{13}C NMR spectrum in D_2O showed a distinctive resonance at δ 162.0 which is assigned to the carboxylate carbon (compare δ 177 for CH_3CO_2H and δ 182 for $CH_3CO_2^-$).[23]

The lithium carboxylate is highly soluble in water, and addition of equimolar aqueous solutions of the dicarbonyl cation **1b** and the lithium salt of the carboxylate anion **4b** slowly precipitates the hydroxycarbonyl **2b** as expected from eq 3. In aqueous solution, **4b** appears to be indefinitely stable at room temperature without the need for added hydroxide but, at 41–43 °C, rapid decomposition occurs to give the hydride **3b**.[24] The solid lithium salt is considerably more stable, a suspension in boiling hexanes (68–70 °C) being recovered unchanged after 2 h (any hydride formed would have been evident immediately from its hexane solubility). In boiling toluene (110 °C) (in which it is partly soluble) the hydride **3b** (30–40%) and some decomposition were observed after 2 h. By contrast, the hydride is rapidly formed at room temperature when the lithium salt is dissolved in THF, diethyl ether or acetone, all of which had been dried by normal laboratory methods. Even though the Nujol IR spectra of samples of these salts prepared in a drybox do not exhibit evident water absorption bands, we suspect that the necessary hydrogen must originate from sufficient water in either the sample or the solvent. The isolation and purification (from alkali hydroxide) of the lithium and calcium salts is then seen to have been crucially dependent on discovering a solvent (i.e., CH_2Cl_2) into which they are extractable without quickly decomposing to hydride.[25-27] When the CH_2Cl_2 solution is treated with water, the yellow carboxylate extracts completely into the aqueous phase, where the carboxylate appears to be especially stabilized, perhaps by hydrogen bonding with water.

Turning now to the pentamethylcyclopentadienyl compounds, the addition of excess LiOH, NaOH, or KOH to the dicarbonyl cation **7** in water gave a yellow aqueous solution presumed to contain the carboxylate, but in each case this extracted completely into CH_2Cl_2 (recall that carboxylates **4** partition preferentially into water). Removal of the CH_2Cl_2 gave a yellow residue. In the case of NaOH or KOH this residue was now *insoluble* in water and was identified spectroscopically as the hydride (η-C_5Me_5)ReH(CO)(*p*-$N_2C_6H_4OMe$) (**9**). In the case of LiOH the solid (which was *soluble* in water) was characterized as the lithium salt of the carboxylate **10**.[28] Its IR in CH_2Cl_2 has a strong ν(CO) band at 1928 cm^{-1} (compare 1933 cm^{-1} for the hydroxycarbonyl **8** and 1906 cm^{-1} for the hydride **9** in the same solvent) and is some 16 cm^{-1} lower than the corresponding cyclopentadienyl compound.[29] The pure lithium salt of **10** is soluble in water but slowly deprotonates water to generate the insoluble hydroxycarbonyl **8** (eq 4). Thus, the more electron-releasing (η-C_5Me_5) group significantly increases the basicity of the anion **10** over that of **4b**, such that **10** is maintained in aqueous solution only in the presence of excess hydroxide ion. The ^1H NMR spectrum of the anion could be obtained in D_2O quickly without added OH^- and matches with that produced by dissolving the cation **7** in NaOD–D_2O. The lithium salt is stable in dry CH_2Cl_2 solution, only minor decomposition to give the dinitrogen complex (η-

$$[(C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]^- + H_2O \rightarrow (C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(COOH) + OH^- \quad (4)$$

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[22] In other variations of the synthesis: (a) a CH_2Cl_2 solution of **1b** reacted slowly with solid LiOH to give the lithium carboxylate in solution with no formation of hydride **3b**; (b) a CH_2Cl_2 solution of **1b** reacted rapidly with aqueous concentrated LiOH to give the Li carboxylate in the aqueous phase and a trace of both the hydride **3b** and (η-C_5H_5)Re(CO)$_2$(N_2) in the CH_2Cl_2 layer.

[23] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 295.

[24] An aqueous solution of the Na salt of **4b**, formed by 1:1 addition of aqueous NaOH and the hydroxycarbonyl **2b** likewise decomposed to hydride **3b** at about 45 °C.

[25] After 24 h of stirring in CH_2Cl_2 at room temperature, the Li salt of **4b** showed IR evidence of a small amount of hydride **3b**. The calcium salt is even more stable.

[26] Chloroform is unsuitable since it reacts rapidly with the Li salt of **4b** to give the chloro complex (η-C_5H_5)ReCl(CO)(*p*-$N_2C_6H_4OMe$) and a small amount of (η-C_5H_5)Re(CO)$_2$(N_2). Notably, the ^1H NMR of the Li salt in $CDCl_3$ is initially extremely broad, becoming less so with time and eventually gives the normal sharp spectrum of the above products. We presume the broadness arises from transient paramagnetic radicals.[27] Because of it we could not observe whether the hydride **3b** is formed prior to the chloro complex. It is known that solutions of the hydride **3b**, while stable enough for immediate ^1H NMR in $CDCl_3$, do gradually convert to the chloro compound.

[27] GC–MS of the $CDCl_3$ solution showed the presence of 1,2-$C_2D_2Cl_4$, $C_6H_4DOCH_3$, (η-C_5H_5)Re(CO)$_2$(N_2), and (η-C_5H_5)ReCl(CO)(*p*-$N_2C_6H_4OMe$).

[28] (a) If CH_2Cl_2 is omitted and the water is pumped away from the yellow aqueous solution of the carboxylate formed with excess NaOH or KOH, then an orange-yellow mixture results which is insoluble in hexane (therefore is not the hydride **9**) and is largely insoluble in ether (therefore is not the hydroxycarbonyl **8**). It presumably contains the carboxylate, but when dissolved in THF, it immediately forms the hydride **9** (IR and subsequent properties). (b) No calcium salt could be synthesized because an aqueous suspension of $Ca(OH)_2$ is not sufficiently basic to transform **7** beyond the hydroxycarbonyl **8** stage.

[29] The ν(CO) or ν(NN) positions for the authentic carboxylate **10** (i.e., the lithium salt) and the hydroxycarbonyl **8** are quite close in most solvents and are most conveniently distinguished in THF. **10**: ν(CO) 1907; ν(NN) 1612 cm^{-1} **8**: ν(CO) 1928; ν(NN) 1620 cm^{-1}.

$C_5Me_5)Re(CO)_2(N_2)$[30] occurring in 1 h. In THF, the lithium salt is at first stable (compare Na or K compounds, above) but the spectrum of the anion (ν(CO) 1907 cm^{-1}, ν(NN) 1612 cm^{-1}) kept in a solution IR cell slowly shows increasing absorption from the carboxylic acid **8** (ν(CO) 1927 cm^{-1}) with time, and it ultimately decomposes into this and a small amount of the dinitrogen complex. Thus the lithium salt of **10** appears not to generate the hydride **9** in solvents under any of the mild conditions that we have tried.

Hydride Complexes (η-C_5H_5)ReH(CO)(*p*-$N_2C_6H_4R$) (3a–c) and (η-C_5Me_5)ReH(CO)(*p*-$N_2C_6H_4OMe$) (9). High yields of the cyclopentadienylrhenium hydrides **3a–c** were obtained by the addition of excess 5 M aqueous *potassium* hydroxide to a rapidly stirred suspension of **1a–c** in diethyl ether. The neutral hydrides extracted into the ether layer and **3b** could be obtained from pentane as a low melting yellow solid and was fully characterized; the remainder were oily and were characterized spectroscopically. The dinitrogen complex (η-C_5H_5)$Re(CO)_2(N_2)$ was also produced in varying amount which decreased with R = Me > OMe >> NEt_2. It is to be recalled that if instead of this procedure, excess hydroxide was added in the aqueous synthesis of the hydroxycarbonyls or to an aqueous suspension of the insoluble hydroxycarbonyls *before* addition of the ether, then, as mentioned above, the hydroxycarbonyls dissolved to give bright yellow, stable aqueous solutions of the anionic carboxylates **4**. Thereupon, no material extracted into the ether (into which the hydrides are known readily to extract) and none extracted into CH_2Cl_2 (into which the hydroxycarbonyls also readily extract), demonstrating neither the hydride nor hydroxycarbonyl to be present under these conditions.

Replacing KOH by NaOH is enough to reduce the efficiency of the hydride synthesis, in part due to the increased stabilization of the carboxylate complex in aqueous solution with the smaller alkali cation.

In the case of the pentamethylcyclopentadienyl complex **7**, the behavior toward excess hydroxide is again different. Addition of either 5 M aqueous NaOH or KOH in excess to a stirred suspension of the aryldiazenido complex **7** in diethyl ether gave an immediate orange aqueous solution from which virtually nothing extracted into the ether layer. Consequently, the synthesis was carried out in CH_2Cl_2–water, whereupon all the rhenium extracts into the CH_2Cl_2 layer (see above). Removal of solvent and extraction with THF, CH_3CN, or acetone removed the rhenium complex, but the IR of these solutions showed them now to consist of the hydride **9**.

An alternative but less convenient method of synthesis of hydrides **3b** and **9** is from $NaBH_4$ and the acetonitrile complex cations **6b** or **12**. Replacement of the labile CH_3CN ligand by hydride occurs largely in preference to hydride attack at the aryldiazenide group. This is notably different from the parent dicarbonyl cations **1** or **7** in which carbonyl substitution normally does not occur, and borohydride reacts preferentially at the diazenide group to give the corresponding aryldiazene complexes (η-C_5H_5)$Re(CO)_2$(NHNAr)[2] and the dinitrogen complexes (η-C_5H_5)$Re(CO)_2(N_2)$[2] and (η-C_5Me_5)$Re(CO)_2(N_2)$.[30]

The presence of the hydride ligand is indicated by the upfield ^{1}H NMR resonance near δ −7 for **3a–c** and δ −5.9 for **9**. This resonance is generally broad and in compound **3** is rather more so in **3b** and **3c** than in **3a**; also the aryl proton resonance for **3b**, **3c**, and **9** is not the usual AA′BB′ pattern normally observed in these 1,4-disubstituted benzene derivatives. The H_α protons (i.e., the protons α to the CNN skeleton) appear as a broad doublet in **3b** and **9** and as a very broad unresolved peak in **3c**. Irradiation of ReH leaves this unchanged in **3b**, so it is not a result of coupling to the hydride. The broadening of this and ReH may be rhenium quadrupolar in origin.[8] In the IR, the compounds exhibit ν(CO) near 1940 (**3a–c**) and 1925 cm^{-1} (**9**) and ν(NN) near 1640 (**3a–c**) and 1619 cm^{-1} (**9**) in hexanes. The ν(NN) absorption shows the expected isotopic shift from 1627 to 1610 cm^{-1} for **3c** ($^{15}N_\alpha$) in CH_2Cl_2, and the values are consistent with the presence of the three-electron-donor singly-bent aryldiazenide group. Mass spectra display the molecular ions as base peaks at *m/e* 400, 416, and 457 (based on ^{187}Re) for **3a–c**, respectively, and *m/e* 486 for **9**. Solutions of the hydride **3b** in hexane or CH_2Cl_2 appear to be quite stable, but in $CHCl_3$ there is slow conversion to the chloro compound (η-C_5H_5)ReCl(CO)(*p*-$N_2C_6H_4OMe$) with ν(CO) at 1950 cm^{-1}. A solution of **3b** in decane at 120 °C showed some precipitation of brown decomposition product, but no additional IR bands. The pentamethylcyclopentadienyl rhenium hydride **9** is similarly stable in hexane, benzene, acetone, or CH_3CN, but it rapidly reacts with $CHCl_3$ or $CHBr_3$ to give the red chloro or bromo complexes (η-C_5Me_5)ReCl(CO)(*p*-$N_2C_6H_4OMe$) (ν(CO) 1924, ν(NN) 1623 cm^{-1} in CH_2Cl_2) and (η-C_5Me_5)ReBr(CO)(*p*-$N_2C_6H_4OMe$) (ν(CO) 1927, ν(NN) 1625 cm^{-1} in CH_2Cl_2).[30]

Dissociation of the Hydroxycarbonyls 2b and 8 in Solution. The foregoing discussion has explained that for both the (η-C_5H_5) and (η-C_5Me_5) rhenium systems it is possible to observe in solution and to isolate and characterize the hydroxycarbonyls **2** and **8** and both the dicarbonyl cations **1** and **7** and the carboxylate anions **4** and **10**. Although they are insoluble in water, the hydroxycarbonyls are very soluble in polar organic solvents, and we were curious to determine what evidence there might be for dissociation in these solvents. A purely organic carboxylic acid RCOOH is well-known to be capable of weak dissociation: $RCOOH \rightleftarrows RCOO^- + H^+$. In the rhenium context this would require dissociation to the carboxylate anion **4** or **10** as in eq 5.

$$(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH) \rightleftarrows H^+ + [(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^- \quad (5)$$

An alternative mode of dissociation of the rhenium hydroxycarbonyl is shown in eq 6. It is simply the reverse

$$(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH) \rightleftarrows [(\eta\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4R)]^+ + OH^- \quad (6)$$

of the method of synthesis from the dicarbonyl cations **1** or **7** and hydroxide. This heterolytic C–O bond fission is not displayed by purely organic carboxylic acids except in strongly acidic media. A third possibility could be dissociation into both cation and anion according to eq 7.

$$\underset{\mathbf{2}}{(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)} \rightleftarrows \underset{\mathbf{1}}{[(\eta\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4R)]} + \underset{\mathbf{4}}{[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-} + H_2O \quad (7)$$

In CH_2Cl_2 solution, the hydroxycarbonyls **2b** and **8** can undergo the same amphoteric behavior observed in water. Bubbling HCl produces the IR spectrum typical of the cations **1b** or **7**, whereas stirring with solid LiOH slowly produces the IR spectrum of the anions **4b** or **10** (note that NaOH or KOH produce the hydride). Thus, dissociation of the hydroxycarbonyl group according to either of eq 5 or 6 can be driven by added H^+ or OH^- in CH_2Cl_2. In-

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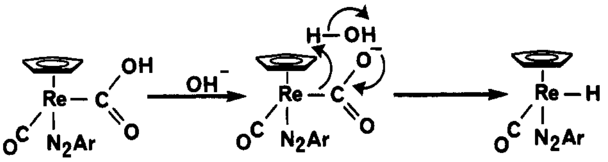
(30) Barrientos-Penna, C. F.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1985**, *4*, 367.

terestingly, when the cation **1b** (as the BF_4 salt) and the lithium carboxylate **4b** are mixed in dry CH_2Cl_2, the resulting IR spectrum is the sum of the IR of the two rhenium species,[31] however, immediately after one drop of water is added, the cation and anion recombine according to eq 7 to generate the spectrum of the hydroxycarbonyl **2b** in CH_2Cl_2 (no hydride is formed) showing this equilibrium position to lay far to the left.

A close examination of the IR spectra of freshly prepared solutions of the hydroxycarbonyls **2b** or **8** in CH_2Cl_2 reveals weak absorptions to be definitely present at positions typical of the ν(CO) and ν(NN) absorptions of the dicarbonyl cations **1b** or **7**.[32] There is also observed a shoulder at ca. 1945 cm^{-1} on the side of the dominant ν(CO) band of the hydroxycarbonyl **2b**, in a position which corresponds to ν(CO) of the anion **4b**. We conclude that the hydroxycarbonyls **2b** and **8** are weakly dissociated in CH_2Cl_2 to furnish the cations **1b** and **7**, but the relative contribution of eq 6 and 7 to this dissociation is presently not known.[33]

Decarboxylation of the Hydroxycarbonyl Complexes 2b and 8. The isolation of the hydroxycarbonyl **2b** has allowed it to be identified positively with the transient intermediate observed when the hydride **3b** is generated by using the dicarbonyl cation **1b** and solid NaOH in CH_2Cl_2 (see earlier). Furthermore, as is required, the hydroxycarbonyl gives the hydride complex quantitatively by IR when its CH_2Cl_2 solution is treated with solid NaOH or KOH. Solutions of the hydroxycarbonyl in other organic solvents such as diethyl ether, THF, or acetone also generate quantitatively the hydride when treated with solid or aqueous NaOH or KOH, and a similar result was obtained for an acetone solution by using only a catalytic amount of Et_3N at room temperature. When base is deliberately excluded, we find that solutions of the hydroxycarbonyl do not decarboxylate and no hydride is observed. Instead, the decomposition products are mainly (η-C_5H_5)Re$(CO)_3$ and (η-C_5H_5)Re$(CO)_2(N_2)$ (and (η-C_5H_5)ReCl(CO)(p-$N_2C_6H_4OMe$) in some chlorinated solvents, e.g., $CHCl_3$).[34]

These results suggest that the actual species undergoing facile decarboxylation in organic solvents under the basic conditions employed is the carboxylate anion **4b**, and the results already presented on the ease with which the hydride **3b** is formed when the authentic lithium salt of the carboxylate anion **4b** is dissolved in most organic solvents supports this idea. Observations using dichloromethane as a solvent indicate that the tendency of the carboxylate anion to decarboxylate is decreased with small or more highly charged cations (Li^+, Ca^{2+}), presumably because these are more effective at removing charge from the carboxylate group in close ion-pair association with it. We envisage, in agreement with Graham and Sweet,[8] the schematic mechanism for the decarboxylation to be as shown in eq 8.



(8)

2 **4** **3**

The pentamethylcyclopentadienyl carboxylate **10** is similarly indicated to be the species which decarboxylates, rather than the actual hydroxycarbonyl **8**, but some differences attributable to the more electron-rich system can be detected. Whereas the lithium salt of the cyclopentadienyl carboxylate **4b** decarboxylates to produce the hydride in THF, the lithium salt of **10** in THF slowly acquires a proton without decarboxylation, to produce the hydroxycarbonyl **8**. In view of this, it appears that the tendency of the anion in **10** to decarboxylate is somewhat less than in **4b**, as might be anticipated if the complex is made rather more electron rich by the C_5Me_5 ligand.

Conclusions

The cations [(η-C_5H_5)Re$(CO)_2(N_2Ar)$]$^+$ (**1**) and [(η-C_5Me_5)Re$(CO)_2$(p-$N_2C_6H_4OMe$)]$^+$ (**7**) are shown to react with a stoichiometric amount of aqueous hydroxide to afford the hydroxycarbonyl complexes (η-C_5H_5)Re(CO)(N_2Ar)(COOH) (**2**) and (η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(COOH) (**8**); both react with excess LiOH and **2** also with $Ca(OH)_2$ to give isolable solid salts of the carboxylate anions [(η-C_5H_5)Re(CO)(N_2Ar)(CO_2)]$^-$ (**4**) and [(η-C_5Me_5)Re(CO)(p-$N_2C_6H_4OMe$)(CO_2)]$^-$ (**10**). When dissolved in a number of polar organic solvents in the presence of water, these anions quickly decarboxylate to give the hydride complexes (η-C_5H_5)ReH(CO)(p-N_2Ar) (**3**) and (η-C_5Me_5)ReH(CO)(p-$N_2C_6H_4OMe$) (**9**). This process is responsible for the apparent decarboxylation of the hydroxycarbonyls **2** and **8** in the presence of base and polar organic solvents, especially where larger cations Na^+, K^+, or Et_4N^+ are present.

Experimental Section

All reactions were carried out under dry nitrogen in Schlenk apparatus connected to a switchable nitrogen/vacuum manifold. Solvents were dried by standard procedures and distilled under nitrogen just prior to use. Analyses were performed by the SFU microanalytical laboratory. Infrared spectra were measured by using Perkin-Elmer 599B or 983 instruments. Mass spectra were obtained by Mr. G. Owen using a Hewlett-Packard Model 5985 using electron-impact (EI) or fast atom bombardment (FAB; Phrasor Scientific, Inc., accessory). NMR spectra were recorded by using Varian XL-100 or Bruker WM400 Fourier Transform instruments.

Preparation of (η-C_5H_5)Re(CO)(p-$N_2C_6H_4CH_3$)(COOH) (2a). A stoichiometric amount of aqueous 0.1 M sodium hydroxide was added dropwise to a suspension of [(η-C_5H_5)Re$(CO)_2$(p-$N_2C_6H_4CH_3$)][BF_4] (**1a**) (100 mg, 0.195 mmol) in water (ca. 10 mL) under continuous stirring, at room temperature. The solution turned yellow-orange from which a yellow solid precipitated. The supernatant solution was pipetted off and the yellow solid washed twice with 3 mL of water and dried under vacuum, yielding complex **2a** (82 mg, 95%) as analytically pure, air-stable, golden yellow microcrystals. IR (CH_2Cl_2, cm^{-1}) 1954 (vs, ν(CO)), 1634 (vs), 1596 (vs, ν(COOH) and ν(NN)); ^1H NMR ($CDCl_3$) δ 2.45 (s, CH_3), 5.83 (s, C_5H_5), 7.25 (s, C_6H_4), 8.9 (br s, COOH). Anal. Calcd for (η-C_5H_5)Re(CO)(p-$N_2C_6H_4CH_3$)(COOH): C, 37.92; H, 2.93; N, 6.32. Found: C, 37.77; H, 2.89; N, 6.27.

Preparation of (η-C_5H_5)Re(CO)(p-$N_2C_6H_4OCH_3$)(COOH) (2b). This was prepared similarly in 95% yield, as a golden yellow,

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[31] To test whether there might also be occurring oxide exchange so as to scramble the cation with the anion, i.e., $MCO^+ + M'CO_2^- \rightleftarrows MCO_2^- + M'CO^+$, we also mixed [($\eta$-$C_5Me_5$)Re$(CO)_2$($p$-$N_2C_6H_4OMe$)][$BF_4$] (**7**) with Li[($\eta$-$C_5H_5$)Re(CO)($p$-$N_2C_6H_4OMe$)($CO_2$)] (**4b**) in CH_2Cl_2. No extra IR bands for the cross cation–anion products were observed showing no oxide exchange to be occurring.

[32] The presence of the cation was also observed by IR for **2b** in acetone, diethyl ether, and THF and for **8** in CH_3CN. Compound **8** is soluble also in benzene and THF, and in these it appears to be undissociated by IR.

[33] There is much less evident absorption from ν(CO) of the carboxylate anion for solutions of the (η-C_5Me_5) rhenium hydroxycarbonyl **8** in CH_2Cl_2, which is consistent with the known increased basicity of this anion compared with the (η-C_5H_5) analogue **4b**.

[34] A sample of **8** in C_6D_6 decomposed completely during an overnight NMR experiment at ambient temperature. The IR and capillary GC–MS (OV-1) of the solution showed the presence of (η-C_5Me_5)Re$(CO)_3$, (η-C_5Me_5)Re$(CO)_2(N_2)$ (M^+ 404, 406 (49%)), $C_6H_5OCH_3$ (M^+ 108 (23)), $C_6D_5C_6H_4OCH_3$ (M^+ 189 (19)), and an unassigned peak of M^+ 134 (10).

air-stable, microcrystalline solid: IR (CH_2Cl_2, cm^{-1}) 1954 (vs, ν(CO)), 1646 (br vs), 1584 (br s, ν(COOH) + ν(NN)); ^{1}H NMR ($CDCl_3$) δ 3.82 (s, OMe), 5.81 (s, C_5H_5), 6.93 (d), 7.36 (d, C_6H_4), 8.4 (br s, COOH); MS (FAB, xenon, sulfolane, based on ^{187}Re), *m/e* 461 (M + H$^+$), 443 (M – OH$^+$), 415 (M – COOH$^+$ or M – OH – CO$^+$). Anal. Calcd for $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OCH_3)(COOH)$: C, 36.60; H, 2.83; N, 6.10. Found: C, 36.65; H, 2.84; N, 6.12.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4NEt_2)(COOH)$ (2c). This was prepared similarly in 96% yield, as a golden yellow, air-stable microcrystalline solid: IR (CH_2Cl_2, cm^{-1}) 1945 (vs, ν(CO)), 1662 (br s), 1632 (br s), 1596 (s, ν(COOH) + ν(NN)); ^{1}H NMR ($CDCl_3$) δ 1.17 (t, CH_3), 3.41 (q, CH_2), 5.80 (s, C_5H_5), 6.66 (d), 7.25 (d, C_6H_4), 7.8 (br s, COOH). Anal. Calcd for $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4NEt_2)(COOH)$: C, 40.80; H, 4.00; N, 8.40. Found: C, 40.72; H, 3.96; N, 8.32.

Preparation of $(\eta\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4OCH_3)$ (3b). To a suspension of **1b** (100 mg, 0.195 mmol) in diethyl ether (10 mL) was added an excess of aqueous KOH (5 mL, 5 M), and the mixture was stirred vigorously at room temperature. The ether layer became yellow, and gas evolution was observed. The ether solution was separated and dried over $CaSO_4$. Filtration and evaporation of the solvent under vacuum afforded an orange oil. An IR spectrum (CH_2Cl_2) of this oil showed that it was a mixture, complex **3a** being the major component, but some $(\eta\text{-}C_5H_5)Re(CO)_2(N_2)$ was also present. This was worked up by two methods. Sublimation of the oily material at room temperature afforded the dinitrogen complex, and then the temperature was increased to 80 °C and the hydride sublimed as an orange-yellow oil in an estimated yield of 80–90%. Alternatively, the oil was extracted with several portions of pentane. The hydride precipitated as a bright yellow solid from pentane at ca. –78 °C; mp 85 °C. Anal. Calcd for **3b**: C, 37.59; H, 3.16; N, 6.75. Found: 37.77; H, 3.19; N, 6.53. Compounds **3a** (R = Me) and **3c** (R = NEt_2) were synthesized similarly but were difficult to solidify and were identified on the basis of their IR, NMR, and mass spectra. IR (hexane, cm^{-1}): **3a** 1946 (vs, ν(CO)), 1637 (s, ν(NN)); **3b** 1944 (vs), 1638 (s). IR (CH_2Cl_2, cm^{-1}): **3a** 1928 (vs, ν(CO)), 1629 (s, ν(NN)); **3b** 1925 (vs), 1630 (s); **3c** 1914 (vs), 1627 (s) (1610 (s, ν(^{15}NN)). ^{1}H NMR (C_6D_6, δ): **3a** – 7.26 (s br, ReH), 2.10 (s, Me), 4.75 (s, C_5H_5), 6.95 (d), 7.52 (d, C_6H_4); **3b** –6.8 (s br, ReH), 3.27 (s, OMe), 4.80 (s, C_5H_5), 6.79 (d), 7.59 (d br, C_6H_4); **3c** –6.7 (s br, ReH), 0.85 (t, CH_3), 2.94 (q, CH_2), 4.87 (s, C_5H_5), 6.53 (d), 7.68 (s br, C_6H_4). MS (EI 70 eV, based on ^{187}Re): **3a** *m/e* 400 (M$^+$), 372 (M – CO$^+$); **3b** *m/e* 416, 388; **3c** *m/e* 457, 429.

Preparation of $Li[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]\cdot CH_2Cl_2$. Method 1. To a suspension of **1b** in water (10 mL) was added an excess of solid LiOH (20 mg), and the mixture was stirred at room temperature. A fast reaction took place and the color of the solution changed from orange-red to bright yellow. Evaporation of the water under reduced pressure gave a yellow solid which was extracted with CH_2Cl_2 to give a bright yellow solution. Addition of hexane gave the product as an air-stable, light yellow solid in quantitative yield, which was further purified by reprecipitation from CH_2Cl_2–hexane. The synthesis works equally well starting with the hydroxycarbonyl complex **2b**.

Method 2. To a suspension of the hydroxycarbonyl **2b** (100 mg, 0.218 mmol) in hexane (10 mL) was added an excess of CH_3Li (0.4 mL, 1.6 M in diethyl ether), and the mixture was stirred vigorously at room temperature. A fast reaction took place and the color of the suspended solid changed from golden yellow to light yellow. Evaporation of the solvent under reduced pressure afforded a light yellow solid in near quantitative yield which was purified by twice reprecipitating from CH_2Cl_2–hexane. CH_2Cl_2 was identified to be present by MS; IR (Nujol, cm^{-1}) 1934 (s, ν(CO)), 1621 (s), 1574 (s br, ν(NN), ν(CO_2)), (CH_2Cl_2, cm^{-1}) 1944 (s, ν(CO)), 1625 (s), 1580 (s br, ν(NN), ν(CO_2)); ^{1}H NMR (D_2O) δ 7.24 (d br), 7.03 (d, 4 H, C_6H_4), 5.82 (s, 5 H, C_5H_5), 3.82 (s, 3 H, OMe); ^{13}C NMR (D_2O) δ 199.8 (CO), 162.0 (CO_2), 95.4 (C_5H_5), 58.6 (OMe). Anal. Calcd for $Li[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]\cdot CH_2Cl_2$: C, 32.73; H, 2.55; N 5.09. Found: C, 32.24; H, 2.53; N, 5.11. Treatment of **2b** with excess NaOD in D_2O produced a yellow solution of the carboxylate anion with ^{1}H NMR parameters δ 7.28 (d br), 7.05 (d, 4 H, C_6H_4), 5.89 (s, 5 H, C_5H_5), 3.87 (s, 3 H, OMe) virtually identical with those of the lithium and calcium salts.

Preparation of $Ca[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO)_2]_2\cdot 2CH_2Cl_2$. This was prepared in similar fashion to the lithium salt by reaction of **1b** with an excess of solid calcium hydroxide in water. The resulting yellow solution was worked up in the same way and gave a near quantitative yield of the product from CH_2Cl_2–hexane: it decomposes near 130 °C; IR (CH_2Cl_2, cm^{-1}): 1940 (s, ν(CO)), 1625 (s), 1580 (s br, ν(NN) and ν(CO_2)); ^{1}H NMR (D_2O) δ 7.25 (d br), 7.01 (d, 4 H, C_6H_4), 5.83 (s, 5 H, C_5H_5), 3.83 (s, 3 H, OMe); CH_2Cl_2 was observed to be present by MS. Anal. Calcd for $Ca[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(CO_2)]_2\cdot 2CH_2Cl_2$: C, 31.97, H, 2.49; N, 4.97. Found: C, 31.73; H, 2.53; N, 5.05.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(OCHO)$ (5). The acetonitrile complex $[(\eta\text{-}C_5H_5)Re(CO)(CH_3CN)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**6**) (80 mg) in acetone (5 mL) was stirred with an excess of finely ground sodium formate. The reaction was followed by IR spectroscopy until all **6** reacted (ca. 2 h). Solvent was pumped off and the residue extracted with dichloromethane and then filtered through Celite. Evaporation of the solvent gave a deep red oil, which could be crystallized by addition of pentane at low temperature, but at room temperature the crystals became oily again: yield 95%. IR (cm^{-1}) 1946 (s, ν(CO)), 1638 (s br, ν(NN)) (CH_2Cl_2); 1948 (vs), 1645 (vs) (acetone), 1956 (vs), 1658 (vs), 1635 (vs) (ether); ^{1}H NMR ($CDCl_3$) δ 3.83 s, OMe), 5.85 (s, C_5H_5), 6.94 (d), 7.19 (d, C_6H_4), 7.70 (s, OCHO); MS (100 °C, 15 eV, based on ^{187}Re), *m/e* 460 (M$^+$), 432 (M – CO$^+$) in 1:4 ratio, (FAB, xenon, sulfolane) *m/e* 461 (M + H$^+$), 432 (M – CO$^+$), 415 (M – OCHO$^+$ or M – OH – CO$^+$) in near 1:1:1 ratio. Anal. Calcd for $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4OMe)(OCHO)]_3\cdot C_5H_{12}$. C, 38.91; H, 3.54; N, 5.79. Found: C, 39.22; H, 3.25; N, 5.84.

Preparation of $[(\eta\text{-}C_5H_5)Re(CO)(CH_3CN)(p\text{-}N_2C_6H_4OMe)[BF_4]$ (6). Excess iodosobenzene was added to a stirred solution of **1b** (149 mg) in CH_3CN (10 mL). The reaction was monitored by IR until complete (3 h). The solution was filtered through Celite and reduced in volume under vacuum. Addition of ether precipitated the product as an orange solid: mp 135 °C; yield 0.112 g (77%); IR 1977 (vs, ν(CO)), 1690 (vs, ν(NN)) cm^{-1} (CH_2Cl_2), 1972 (vs), 1639 (vs) cm^{-1} (acetone); ^{1}H NMR ($CDCl_3$) δ 3.02 (s, CH_3CN), 3.89 (s, OMe), 6.13 (s, $\eta\text{-}C_5H_5$), 7.03 (d), 7.17 (d, aryl); MS (FAB, sulfolane, xenon, based on ^{187}Re), *m/e* 456 (M$^+$ of cation), 415 (M$^+$ – MeCN).

Preparation of $[(\eta\text{-}C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (7). $(\eta\text{-}C_5Me_5)Re(CO)_3$ (1.10 g, 2.71 mmol) was irradiated in freshly distilled THF (400 mL) under argon for 180 min using a quartz immersion-type reactor and a 200-W Hanovia high-pressure mercury source. The solution was concentrated to one-third volume, and then $[p\text{-}N_2C_6H_4OMe][BF_4]$ (0.46 g, 2.07 mmol) in acetone (15 mL) was added dropwise with continuous stirring at room temperature. The solution changed from yellow-brown to dark red. After 1 h of stirring, the solution was concentrated to 50 mL by rotary evaporation and then diethyl ether was added slowly. A maroon solid appeared after a few minutes. Supernatant solvent was removed by pipet and the solid washed twice with diethyl ether: yield 76% of maroon microcrystals; mp 128–130 °C; IR (CH_2Cl_2) 2051 (vs), 1995 (vs, ν(CO)), 1736 (s) cm^{-1} (ν(NN)); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 15 H, C_5Me_5), 3.92 s, 3 H, OMe), 7.14 (d, 2 H), 7.38 (d, 2 H, C_6H_4); MS (FAB, sulfolane, xenon, based on ^{187}Re), *m/e* 513 (M$^+$ of cation). Anal. Calcd for **7**: C, 38.06; H, 3.67; N, 4.67. Found: C, 38.11; H, 3.45; N, 4.53.

Preparation of $(\eta\text{-}C_5Me_5)Re(CO)(COOH)(p\text{-}N_2C_6H_4OMe)$ (8). A suspension of **7** (50 mg) in water (15 mL), in which it is slightly soluble, was vigorously stirred, and then aqueous 0.10 M NaOH (0.83 mL) was added very slowly. The golden yellow solid which precipitated quantitatively was washed twice with cold water and then dried under vacuum. It decomposed at 90–95 °C without melting. IR (1933 (vs, ν(CO)), 1623 (s), 1587 (m br) cm^{-1} (ν(NN) + ν(COOH)) (CH_2Cl_2), 1934 (vs), 1620 (s), 1585 (m br) cm^{-1} (benzene); ^{1}H NMR (acetone-d_6) δ 2.11 (s, 15 H, C_5Me_5), 3.82 (s, 3 H, OMe), 6.96 (d, 2 H), 7.49 (d, 2 H, C_6H_4), 9.41 (br s, 1 H, COOH); MS (FAB, xenon, sulfolane), *m/e* 511, 513 (M – OH$^+$); 483, 485 (vw, M – COOH$^+$ or M – OH – CO$^+$); MS (EI, 70 eV), *m/e* 484, 486 (M – $CO_2$$^+$). Anal. Calcd for **8**: C, 43.10; H, 4.34; N, 5.29. Found: C, 43.00; H, 4.10; N, 5.09.

Preparation of $(\eta\text{-}C_5Me_5)ReH(CO)(p\text{-}N_2C_6H_4OMe)$ (9). Compound **7** (50 mg) was dissolved in CH_2Cl_2 (15 mL), and an excess (ca. 2 mL) of aqueous 6 M NaOH was added while vigorously stirring. The CH_2Cl_2 layer became yellow-orange. Solvent was removed by pumping at room temperature. The residue was dissolved in THF (it is insoluble in hexane) and filtered through Celite to give an orange solution, having ν(CO) at 1910 (vs) cm^{-1} and ν(NN) at 1615 (s) cm^{-1}. The THF was pumped off and the oily residue was now easily extracted into hexane to give an orange solution having ν(CO) 1925 (vs) and ν(NN) 1619 (s) cm^{-1}. The hexane solution was chromatographed on neutral alumina. Elution with benzene gave a yellow solution. Benzene was pumped off, and the yellow residue was dissolved in pentane from which **8** precipitated as a yellow solid during 6 h at −78 °C in 80% yield: decomposes at 95–98 °C; IR (hexane) 1925 (vs, ν(CO)), 1619 (s) cm^{-1} (ν(NN), (CH_2Cl_2) 1906 (vs), 1618 (s) cm^{-1}; ^1H NMR (C_6D_6) δ −5.88 (s, 1 H, ReH), 1.90 (s, 15 H, C_5Me_5), 3.27 (s, 3 H, OMe), 6.78 (d, 2 H), 7.61 (d, 2 H, C_6H_4); MS (16 eV), *m/e* 484, 486 (M^+) 456, 458 ($M - CO^+$). Anal. Calcd for **9**: C, 44.53; H, 4.74; N, 5.77. Found: C, 45.44; H, 5.23; N, 5.71.

Preparation of Li[(η-C_5Me_5)Re(CO)(*p*-$N_2C_6H_4OMe$)(CO_2)]. Method 1. The hydroxycarbonyl **8** (100 mg) was suspended in hexane (25 mL) and excess (0.5 mL) of MeLi (1.6 M in diethyl ether) was added under N_2 with vigorous stirring. After 30 min the solvent was removed by pipet and the yellow solid washed twice with 5 mL of hexane. It was redissolved in CH_2Cl_2, filtered under N_2, and reprecipitated by adding hexane as a yellow solid in near quantitative yield: CH_2Cl_2 was observed to be present by MS; IR (CH_2Cl_2, cm^{-1}) 1928 (vs, ν(CO)), 1614 (s, ν(NN)), (THF) 1907 (vs), 1612 (s); ^1H NMR (D_2O) δ 2.03 (15 H, C_5Me_5), 3.81 (s, 3 H, OMe), 7.02 (d, 2 H), 7.28 (d, 2 H, C_6H_4). Anal. Calcd for Li[(η-C_5Me_5)Re(CO)(*p*-$N_2C_6H_4OMe$)(CO_2)]·CH_2Cl_2: C, 38.77; H, 3.88; N, 4.52. Found: C, 38.32; H, 4.18; N, 4.76.

Method 2. The dicarbonyl [(η-C_5Me_5)Re$(CO)_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (**7**) was dissolved in CH_2Cl_2 and stirred with an excess of saturated aqueous LiOH. Within a few minutes the CH_2Cl_2 layer became orange-yellow. This was separated from the colorless aqueous layer by pipet and solvent removed to give the product as a yellow solid (soluble in water and insoluble in hexane) in quantitative yield.

Treatment of **7** with excess NaOD in D_2O produced a yellow solution of the carboxylate anion with ^1H NMR parameters δ 2.00 (15 H, C_5Me_5), 3.79 (3 H, OMe), 7.00 (d, 2 H), 7.26 (d, 2 H, C_6H_4) virtually identical with those of the lithium salt.

Preparation of (η-C_5Me_5)Re(CO)(*p*-$N_2C_6H_4OMe$)(OCHO) (11). Compound **12** (70 mg) in acetone (25 mL) was stirred with finely ground solid sodium formate, then water (10 mL) was added, and the reaction was followed by IR. All of **12** had reacted in 1 h. Solvent was pumped off, and the residual water was pipetted from the red-orange product which was then dissolved in ether and filtered through Celite. Addition of hexane precipitated a red-orange solid: mp 65–67 °C; 85% yield; IR (acetone) 1931 (vs, ν(CO)), 1645 (m), 1620 (s) cm^{-1}, (ether) 1941 (vs), 1648 (m), 1622 (s) cm^{-1}, (CH_2Cl_2) 1925 (vs), 1642 (m), 1624 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (s, 15 H, C_5Me_5), 3.81 (s, 3 H, OMe), 6.92 (d, 2 H), 7.29 (d, 2 H, C_6H_4), 8.03 (s, 1 H, OCHO), (C_6D_6) δ 1.73 (s), 3.22 (s), 6.74 (d), 7.63 (d), 8.37 (s); MS (EI, 15 eV, 75 °C, based on ^{187}Re), *m/e* 530 (M^+), 502 ($M - CO^+$), 486 ($M - CO_2^+$) in 1:5:3 ratio; MS (FAB, xenon, sulfolane, based on ^{187}Re), *m/e* 513 ($M - OH^+$), 502 ($M - CO^+$), 485 ($M - HCO_2^+$), 429 ($M - N_2 - CO - HCO_2^+$). Anal. Calcd for **11**: C, 43.10; H, 4.34; N, 5.29. Found: C, 43.53; H, 4.40; N, 5.34.

Preparation of [(η-C_5Me_5)Re(CO)(CH_3CN)(*p*-$N_2C_6H_4OMe$)][BF_1] (12). An approximate 20% stoichiometric excess of iodosobenzene was added as a solid to a stirred solution of **7** (50 mg) in CH_3CN (15 mL). After 30 min, all of **7** had reacted (by IR) and no further change occurred. Removal of solvent under vacuum gave a red oily solid which was recrystallized from acetone–ether as an orange microcrystalline solid: mp 65–67 °C; 91% yield; IR (acetone) 1958 (vs, ν(CO)), 1655 (s, ν(NN)), (CH_3CN) 1959 (vs), 1658 (s), (CH_2Cl_2) 1962 (vs), 1658 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (s, 15 H, C_5Me_5), 3.10 (s, 3 H, CH_3CN), 3.85 (s, 3 H, OMe), 7.05 (d, 2 H), 7.24 (d, 2 H, C_6H_4); MS (FAB), sulfolane, xenon, based on ^{187}Re), *m/e* 526 (M^+ of cation), 485 ($M^+ - MeCN$). Anal. Calcd for **12**: C, 39.21; H, 4.08; N, 6.86. Found: C, 38.77; H, 4.18; N, 6.63.

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Registry No. 1a, 81028-25-3; **1b**, 81028-27-5; **1c**, 81028-31-1; **2a**, 86688-81-5; **2b**, 86688-82-6; **2c**, 86688-83-7; **3a**, 86688-84-8; **3b**, 86688-85-9; **3c**, 86688-86-0; **4b**, 94405-77-3; **4b**·Li, 94405-76-2; **4b**·Ca, 94405-78-4; **5**, 94405-79-5; **6**, 94405-81-9; **7**, 92786-90-8; **8**, 94405-82-0; **9**, 94405-83-1; **10b**, 94405-85-3; **10b**·Li, 94405-84-2; **11**, 94405-86-4; **12**, 94405-88-6; (η-C_5H_5)Re$(CO)_2$(Na), 36543-62-1; (η-C_5Me_5)Re$(CO)_3$, 12130-88-0; [*p*-$N_2C_6H_4OMe$][BF_4], 459-64-3; iodosobenzene, 536-80-1.

New Structural Forms of Alkynylplatinum(II) Complexes with $R_2PCH_2PR_2$ Ligands

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The complexes [$PtCl_2$(L-L)] react with $MeC\equiv CH$ and NaOR in ROH to give the monomeric, bis(acetylide) compounds [$Pt(C\equiv CMe)_2$(L-L)]. (L-L = depm and dippm, R = Et; L-L = dppm, R = Me). [$Pt_2Cl_4(dmpm)_2$] reacts with $MeC\equiv CH$ and NaOMe in MeOH to give the dimeric acetylide complex *cis,cis*-[$Pt_2(C\equiv CMe)_4(dmpm)_2$]. The complex [$Pt(C\equiv CMe)_2$(dppm)] rearranges in solution to give *trans,trans*-[$Pt_2(C\equiv CMe)_4(dppm)_2$], catalyzed by a trace amount of dppm, while [$Pt(C\equiv CMe)_2$(depm)] rearranges to a mixture of all three possible isomers of [$Pt_2(C\equiv CMe)_4(depm)_2$] (i.e., cis,cis, cis,trans, and trans,trans), catalyzed by PPh_3. Addition of PPh_3 to [$Pt(C\equiv CMe)_2$(dippm)] leads only to decomposition. All products are characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy and, in some cases, by elemental analysis.

Introduction

There has recently been interest in [bis(diphenylphosphino)methane]platinum acetylide complexes.[1-3] Reaction of [$PtCl_2$(dppm)] with $LiC\equiv CR$ produced the "face-to-face" diplatinum complexes of the type *trans,*-

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