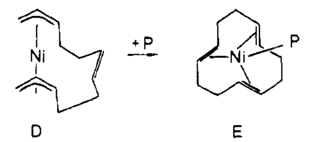
Scheme II



Coupling of the terminal carbon atoms of the two η^3-pentadienyl ligands in C leads to the isolated product 1.

Although this proposed mechanism is speculative, several of its steps have precedent in the nickel-catalyzed butadiene cyclotrimerization reaction studied by Wilke.[14] In the nickel system, the *anti,anti*-bis(η^3-allyl-C_{12})nickel complex, D in Scheme II, can be isolated. Upon addition of trialkylphosphine, the two allylic moieties couple, and the cyclododecatriene ligand of the isolated cyclododecatriene(trialkylphosphine)nickel product E possesses three trans double bonds. The stereochemistry of the cyclododecatriene ligand implies that the *anti,anti*-bis-(η^3-allyl-C_{12})nickel complex, D, converts to its syn,syn isomer before the coupling of the allylic ligands occurs.

Compound 1 reacts with mild oxidizing agents such as $AgPF_6$ to form isolable cationic complexes in the absence or presence of Lewis bases. The chemistry of these cations will be reported in a future communication.

The manganese-centered pentadienyl coupling reaction reported here illustrates the versatility of the acyclic pentadienyl ligand and the rich reaction chemistry that results from the pentadienyl ligand's ability to adopt a variety of bonding modes. We are continuing to investigate this and other pentadienylmetal-phosphine reaction systems.

Acknowledgment. We gratefully acknowledge Research Corp. for providing the funds (Cottrell Research Grant to J.R.B.) to purchase an inert atmosphere drybox. We thank Professor G. G. Stanley for assistance with the single-crystal X-ray diffraction study of 1 and R. A. Berger for his help in obtaining the mass spectrum of 1.

Registry No. 1, 86508-10-3; $MnBr_2$, 13446-03-2; potassium 2,4-dimethylpentadienide, 74205-98-4.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Aryldiazenido Complexes. Hydroxycarbonyl and Hydrido Derivatives of the Dicarbonyl-(η-cyclopentadienyl)(aryldiazenido)rhenium Cation

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Received May 2, 1983

Summary: The cationic aryldiazenido complexes [(η-C_5H_5)Re(CO)$_2$(p-$N_2C_6H_4R$)][BF_4] (R = Me, OMe, or NEt_2) react with equimolar aqueous 0.1 M NaOH to give the air-stable, microcrystalline hydroxycarbonyl complexes (or metallocarboxylic acids) (η-C_5H_5)Re(CO)(p-$N_2C_6H_4R$)-(COOH) and with excess 5 M KOH in H_2O-diethyl ether to give the air-stable hydrido complexes (η-C_5H_5)ReH(CO)-(p-$N_2C_6H_4R$). These new hydroxycarbonyl and hydrido complexes are aryldiazenido analogues of the nitrosyl compounds (η-C_5H_5)Re(CO)(NO)(COOH) and (η-C_5H_5)ReH-(CO)(NO) recently reported to be formed by action of base on the cationic complex [(η-C_5H_5)Re(CO)$_2$(NO)]-[BF_4] and exhibit comparable stability and spectroscopic properties, suggesting a similar influence of the nitrosyl and aryldiazenido ligands in the two series.

The corresponding complex cations [(η-C_5H_5)Re(CO)$_2$-(NO)]$^+$ (1) and [(η-C_5H_5)Re(CO)$_2$(N_2Ar)]$^+$ (2) (Ar = aryl) potentially offer a good opportunity to compare the properties of the nitrosyl and aryldiazenido (N_2Ar) ligands and their influence on the reactions of the dicarbonyl(η-cyclopentadienyl)rhenium group. This is provided, of course, that the ligand itself is not the site of reaction. Unfortunately, in several reactions of 2 this happens to be the case. A particularly striking example is the action of $NaBH_4$, which converts 2 to the dicarbonyl aryldiazene complex (η-C_5H_5)Re(CO)$_2$(NHNAr), whereas in 1 a carbonyl group is reduced, leaving the nitrosyl group intact.[1,2]

In view of this, we now wish to report the reactions of **2a-c** with hydroxide ion, where we have observed a close correspondence with the chemistry recently reported by Sweet and Graham[3] for 1. Furthermore, under appropriate conditions the products are, similarly, isolable, stable hydroxycarbonyl complexes, MCO_2H (or metallocarboxylic acids) which are therefore of considerable interest in view of the present scarcity of well-characterized compounds containing this functional group.[2d,3-8]

These new hydroxycarbonyl complexes (η-C_5H_5)Re-(CO)(N_2Ar)(COOH) (**3a-c**) were synthesized by the dropwise addition under nitrogen of an equimolar quantity of aqueous 0.1 M NaOH to a stirred suspension of **2a-c** in water at room temperature. This gave yellow-orange solutions from which the products **3a-c** precipitated as analytically pure, golden yellow, air-stable, microcrystalline solids in ca. 95% yield,[9a] which are slightly soluble in water, giving bright yellow solutions. Their spectroscopic properties are those expected for formulation as hydroxycarbonyl complexes and compare with those of (η-C_5H_5)-Re(CO)(NO)(COOH).[3] A strong terminal ν(CO) band

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(2) (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. (c) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1578. (d) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *Ibid.* **1979**, *101*, 741.
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(9) For example, **3a**: mp 102-104 °C dec; IR (CH_2Cl_2) 1954 (vs) (ν(CO)), 1643 (vs), 1596 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H, CH_3), 5.83 (s, 5 H, C_5H_5), 7.25 (s, 4 H, C_6H_4), 8.9 (br s, 1 H, COOH). Anal. Calcd for $C_{14}H_{13}N_2O_3Re$: C, 37.92; H, 2.93; N, 6.32. Found: C, 37.77; H, 2.89; N, 6.27. ν(OH) was not observable directly in CH_2Cl_2, fluorolube mull, or KBr spectra of **3a-c**; ν(OD) was observed as a medium-weak broad band at 2240 cm^{-1} in a fluorolube mull spectrum of **3c** synthesized from NaOD in D_2O, giving a calculated ν(OH) near 3150 cm^{-1}. A weak band near 3450 cm^{-1} in **3a-c** showed no deuterium exchange.

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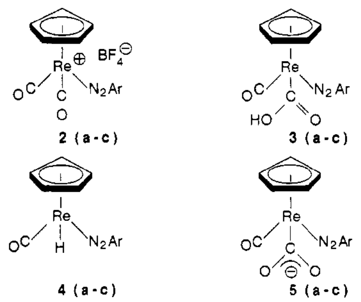
occurs at about 1950 cm^{-1}. Two or three broad bands occur in the region 1550–1660 cm^{-1} assigned to ν(NN) of the expected singly bent N_2Ar group and to ν(CO) and δ(COH) of the carbonyl group; these modes are strongly coupled, with the result that isotopic substitution by ^{15}N (96%) at the metal-bound nitrogen atom (N_α) causes all the bands to move to lower wavenumber and no band can be individually assigned to ν(NN). In the ^1H NMR spectrum resonances assigned to the η-C_5H_5 and CO_2H groups occur near δ 5.8 and 8.9, respectively, positions close to those observed for (η-C_5H_5)Re(CO)(NO)(COOH).[3] The resonance of the carboxylic proton also agrees well with the reported value for *trans*-$PtCl(PEt_3)_2$(COOH) (δ 8.5 in CD_3CN).[7,9b]

Although mass spectral analyses did not result in molecular ion peaks even when a low electron voltage (12 eV) and a low temperature (ion source = 40 °C) were used, results were obtained that might be expected from thermal decomposition of **3**. Thus, for **3a**, time profiles of 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-$N_2C_6H_4CH_3$)] during the analysis were closely similar, indicating thermal decarboxylation of the hydroxycarbonyl complex to the corresponding hydrido complex to be occurring during the runs.

These hydrido complexes (η-C_5H_5)ReH(CO)(p-$N_2C_6H_4R$) (**4a**–**c**) could be synthesized independently by the addition of *excess* aqueous 5 M KOH to a vigorously stirred suspension of **2a**–**c** in diethyl ether at room temperature under nitrogen. All were yellow air-stable oily liquids at room temperature that could be separated by sublimation from the dinitrogen complex (η-C_5H_5)Re$(CO)_2(N_2)$ when this was also formed.[10] All show in the IR (CH_2Cl_2) strong bands at about 1925 and 1630 cm^{-1} due to ν(CO) and ν(NN) of the expected singly bent N_2Ar ligand, respectively[11,12] (cf. ν(CO) 1980 cm^{-1} and ν(NO) 1723 cm^{-1} for (η-C_5H_5)ReH(CO)(NO)). In the ^1H NMR the hydride signal occurs near δ −7.0 as a singlet[13] that is broader in **4b** and **4c** than in **4a** (cf. δ −8.50 for (η-C_5H_5)ReH(CO)(NO)). MS analysis showed molecular ions for **4a**–**c** as the base peaks.



Ar = (a) p-C_6H_4Me

(b) p-C_6H_4OMe

(c) p-$C_6H_4NEt_2$

(10) For example, **4a**: Excess aqueous 5 M KOH was added to a rapidly stirred suspension of **2a** in diethyl ether. The ether layer became yellow and vigorous evolution of CO_2 occurred. The ether solution was separated, dried over $CaSO_4$, filtered, and evaporated under vacuum to give an orange oil containing mainly **4a**, with some (η-C_5H_5)$Re(CO)_2N_2$ (by IR). The latter was removed by vacuum sublimation at room temperature (ca. 20–30% yield); vacuum sublimation at 80 °C gave **4a** as an orange-yellow oil (ca. 70% yield): IR (CH_2Cl_2) 1928 (vs) (ν(CO)), 1629 (vs) (ν(NN)) cm^{-1}; ^1H NMR (C_6D_6) δ −7.26 (br s, 1 H, ReH), 2.10 (s, 3 H, CH_3), 4.75 (s, 5 H, C_5H_5), 6.95, 7.52 (AA′BB′q, 4 H, C_6H_4); mass spectrum, M^+, $(M - CO)^+$.

(11) ^{15}N isotopic shift of ν(NN): **4c**–$^{15}N_\alpha$ ν(NN) 1610 cm^{-1}.

(12) Weak bands assigned to ν(ReH) occur at 2025 (**4a**), 2030 (**4b**), and 2033 (**4c**) cm^{-1}; cf. 2011 cm^{-1} (hexane) for (η^5-C_5H_5)ReH(CO)(NO).[3]

As has been suggested for the corresponding nitrosyl system,[3] the function of the excess base in the formation of the hydrido complexes is likely to be deprotonation of the hydroxycarbonyl complexes to give metallocarboxylato intermediates **5a**–**b** that undergo rapid decarboxylation and abstraction of a proton from the protic solvent. Indeed, the pure hydroxycarbonyl complexes **3a**–**c** are smoothly transformed into the hydrido complexes **4a**–**c** by treatment with base and *simultaneous* extraction into ether.[14] In the absence of ether, however, addition of base to an aqueous suspension of the hydroxycarbonyls caused them to rapidly dissolve to give orange-yellow solutions. Thereafter, no material could be subsequently extracted from these solutions into either CH_2Cl_2 (into which the hydroxycarbonyls **3a**–**c** are extractable) or into ether (into which the hydrido complexes **4a**–**c** are extractable). This behavior parallels that observed for the nitrosyl,[3] and we agree with Sweet and Graham that in all probability the solutions contain anionic carboxylato complexes, in this case [(η-C_5H_5)Re(CO)(p-$N_2C_6H_4R$)(COO)]$^-$, **5a**–**c**, which we are currently attempting to isolate and characterize.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada through an operating grant. We thank the University of Concepcion, Concepcion, Chile, for a leave of absence (to C.F.B.).

Registry No. **2a**, 86688-80-4; **2b**, 81028-27-5; **2c**, 81028-31-1; **3a**, 86688-81-5; **3b**, 86688-82-6; **3c**, 86688-83-7; **4a**, 86688-84-8; **4b**, 86688-85-9; **4c**, 86688-86-0.

(13) The aryl proton resonances in **4b** and **4c** are also not the usual AA′BB′ quartet patterns expected for 1,4-disubstituted aromatics. H_α (α to CN_2) is a broad doublet in **4b** and a very broad singlet in **4c**. This is unchanged on irradiating ReH. This and the broadness of ReH may be a result of rhenium quadrupolar relaxation (see ref 3).

(14) The hydroxycarbonyls **3a**–**c** are also observed as transient intermediates that transform to the hydrido complexes **4a**–**c** when solutions of **2a**–**c** in CH_2Cl_2 are treated with solid KOH or NaOH and followed by IR. IR monitoring of solutions of **2a**–**c** in acetone or CH_2Cl_2 that were treated with excess aqueous KOH or NaOH showed the presence of hydrides **4a**–**c** but no absorptions due to hydroxycarbonyl intermediates.

Transition-Metal Ketenes. 18.[1] Synthesis of a Novel Five-Membered Tungsten–Arsenic Heterocycle. Ketene–Ylide Conversion

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Received May 16, 1983

Summary: The addition of trimethylphosphine to the tungsten-coordinated arsinylketene **1** followed by an intramolecular substitution of iodine yields the novel five-membered metallaheterocycle **2**. Preparation and spectroscopic investigations of the new complex are reported.

The first synthesis of phosphorus- and arsenic-substituted ketenes in the coordination sphere of tungsten[2,3] was effected by treating carbonyl (η^5-cyclopentadienyl)(η^2-ketenyl)(trimethylphosphine)tungsten[4] with halo-

(1) Contribution 17: Sieber, W. J.; Eberl, K.; Wolfgruber, M.; Kreissl, F. R. *Z. Naturforsch., B*: *Anorg. Chem., Org. Chem.* in press.

