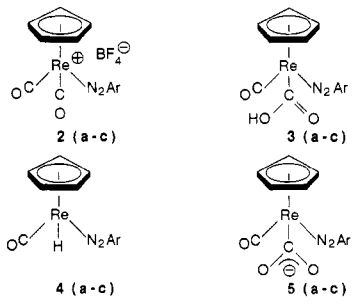
occurs at about 1950 cm^{-1}. Two or three broad bands occur in the region 1550–1660 cm^{-1} assigned to ν(NN) of the expected singly bent N_2Ar group and to ν(CO) and δ(COH) of the carbonyl group; these modes are strongly coupled, with the result that isotopic substitution by ^{15}N (96%) at the metal-bound 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.



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.

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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.

(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]

(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

F. R. Kreissl,* M. Wolfgruber, and W. J. Sieber

Anorganisch-Chemisches Institut der Technischen Universität Müchen D-8046 Garching, Germany

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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-

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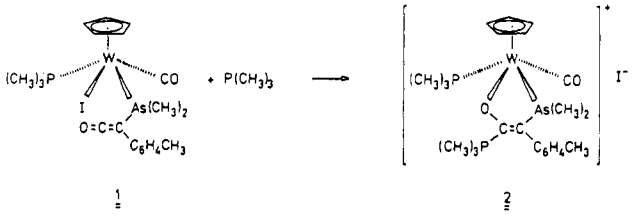
phosphines or -arsines. This interesting addition–rearrangement proceeds, at least in the case of the halophosphines, via isolable intermediates that have a tungsten bicyclobutanone structure.[5] Recent efforts to displace the ketene moiety by trimethylphosphine led, however, to attack by the phosphine at the electrophilic central ketene carbon atom. Concomitant nucleophilic substitution of the tungsten-coordinated iodine by the former ketene oxygen afforded the thermodynamically favored five-membered ring system.



To date very little information is available about the reaction of ketenes with phosphines or phosphite,[6] although the addition of nucleophiles such as alcohols or amines is a common reaction in ketene chemistry.[7] Metal–allenylidene complexes undergo a comparable attack of phosphines at the cumulene chain,[8] which shows electronic features similar to that of the ketene unit.

The deep yellow, diamagnetic complex **2** is moderately soluble in dichloromethane. Its composition and structure were determined by elemental analysis and infrared and proton, carbon-13, and phosphorus NMR spectroscopy, and its ionic character was demonstrated by qualitative conductivity measurements. The infrared spectrum displays in the ν(CO) region (in dichloromethane) the metal carbonyl group at 1782 cm^{-1} (vs). A second absorption at 1565 cm^{-1} (s) can be assigned to the metal enolate function in the ring, in agreement with the corresponding one found in the spectra of acetylacetonate complexes.[9] This rules out a possible but less likely attack of the phosphine at the carbon atom α to the arsenic group. The proton NMR spectrum exhibits two signals for the arsenic methyl groups due to their magnetic nonequivalence in the complex. The ylidic character of the trimethylphosphine group attached to the former ketene carbon is demonstrated by its ^{31}P–^{1}H coupling constant of 14.8 Hz.[10] The ^{31}P NMR spectrum of **2** shows a considerable downfield shift of 20 ppm and an increase of the ^{183}W–^{31}P coupling constant for the metal-coordinated trimethylphosphine compared to the ^{31}P NMR spectrum of **1**. Moreover, there is a singlet for the second trimethylphosphine group at δ 12.4 as expected for an ylidic phosphine.[10] The carbon-13 spectrum also supports the indicated structure of **2**. As in the proton NMR spectrum, the arsenic methyl groups are again magnetically nonequivalent. The chemical shifts and the spin–spin interactions within the As–C(3)=C(4)–P$(CH_3)_3$ unit are especially significant. Thus, the resonance of the PCH_3 carbon atoms (δ 10.0 ($^{1}J(^{31}P–^{13}C)$ = 54.5 Hz)) are best accounted for in terms of an ylidic phosphorus atom.[11–13] The shift parameters of the C(3) and the C(4) carbon atoms indicate their olefinic character, and the large $^{1}J(^{31}P–^{13}C)$ coupling constant of 94.0 Hz resembles that reported by Schmidbaur for H_2C=P$(CH_3)_3$.[12] The further phosphorus–carbon coupling between C(4) and the phosphine ligand is consistent with the cyclic structure of **2**.[14]

[1-Carbonyl-1-(η^5-cyclopentadienyl)-2,2-dimethyl-3-(4-methylphenyl)-4-(trimethylphosphonio)-1-(trimethylphosphine)tungsta-2λ^4-arsa-5-oxa-3-cyclopentene] iodide (**2**) was prepared as follows. At −78 °C 0.1 mL of trimethylphosphine was added to a solution of 0.9 g (1.26 mmol) of the ketene complex **1**. The crude product was precipitated with ether/pentane. Further purification by recrystallization from a mixture of dichloromethane/pentane yielded, after drying under vacuum, 0.95 g (95%) of **2**, a deep yellow powder: ^{1}H NMR (CD_2Cl_2, relative to $CDHCl_2$, 5.4 ppm) δ 7.22 (m, C_6H_4), 5.44 (d, J = 0.9 Hz, C_5H_5), 2.5 (s, CH_3), 1.87 (d, J = 14.8 Hz, $CPCH_3$), 1.75, 1.69 (s, $AsCH_3$), 1.67 (d, J = 10.2 Hz, $WPCH_3$); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, relative to H_3PO_4 external) δ 12.39 (s, $CPCH_3$), −4.94 (s, $WPCH_3$, $^{1}J(^{183}W–^{31}P)$ = 308.2 Hz); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, relative to CD_2Cl_2, 54.2) δ 253.1 (d, J = 20.8 Hz, WCO), 157.6 (dd, J = 94.0 Hz, J = 4.9 Hz, =CP), 138.1–129.6 (C_6H_4), 123.8 (d, J=39.1 Hz, AsC=), 88.9 (C_5H_5), 21.2 (CH_3), 17.3 (d, J = 31.7 Hz, $WPCH_3$), 15.8, 13.6 ($AsCH_3$), 10.0 (d, J = 52.5 Hz, $CPCH_3$). Anal. Calcd for $C_{23}H_{36}AsIO_2P_2W$ (792.16): C, 34.87; H, 4.58; I, 16.02. Found: C, 35.19; H, 4.57; I, 15.79.

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Registry No. 1, 86508-28-3; 2, 86527-02-8.

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(14) The corresponding complex in which the arsenic atom is replaced by a phosphorus atom has also been prepared. In this analogue, it is known from the ^{31}P NMR spectrum that the two phosphorus atoms attached to tungsten are trans to each other. On this basis, structure **2** is assigned with P and As atoms in trans positions.