dicarbide cluster, $(\mu_6\text{-}C_2)_2(Cp^*Fe)_2Ru_6(CO)_{14}(\mu\text{-}CO)_3$ (**3**), were isolated together with another tetranuclear dicarbide cluster, **4**, and Fp^*_2 (Scheme I).[4] Cluster **4**, in which the C_2 ligand is coordinated in a well-established way,[1l,m,2e,5] was also obtained from $Fp^*C{\equiv}CH$ and $Ru_3(CO)_{12}$.[6]

The tetranuclear cluster **2** (Figure 1), in which the C_2 part lies within the range of bonding interaction of the Fe and Ru atoms, is the first example of a permetalated ethene. However, connection of the two vertices of the rectangular tetrametallic framework distorts the structure, as indicated by (1) the elongated Ru-Ru bond [2.963 (2) Å; cf. **3**, 2.72-2.86 Å], (2) the lesser Ru-C1 interaction [2.198 (9) Å; cf. $Cp_2Ru_2(\mu\text{-}CO)(CO)_2(\mu\text{-}C{=}CH_2)$, 2.026 (7) and 2.033 (7) Å[7]], and (3) the slightly twisted $Fe_2Ru_2(\mu_4\text{-}C_2)$ core (the torsion angle Fe-Ru-Ru'-Fe' = 24°). In addition, the C1-C1' length [1.27 (2) Å], which is intermediate between the C-C lengths of **1**[2c] and dinuclear μ-vinylidene complexes [1.30-1.35 Å],[8] suggests triple-bond character still remaining.

The structure of **3** comprises two C_2 ligands and an octametallic framework (Figure 2). Every edge of the Ru_4 square (Ru1-4) is bridged by Fe or Ru, and each C_2 moiety above and below the Ru_4 square interacts with a boat-like hexanuclear array. Such a metal array can be regarded as a finite piece of an fcc or an hcp lattice.[1r] Of the six Ru atoms, Ru5 and Ru6 in the apical positions lie closer to the C_2 ligands. The situation is essentially the same as that in $(\mu_6\text{-}C_2)Co_6(\mu_4\text{-}S)(CO)_{14}$ (**5**),[1r] the only previous example of a $(\mu_6\text{-}C_2)M_6$ cluster with the boat-like metal array. While the C-C distances [C21-C22, 1.35 (4) Å; C23-C24, 1.37 (3) Å] are comparable to that in **5** [1.37 (2) Å], the different sizes of the apical metals cause considerable distortion of the C_2 moieties, as is evident from the M-C-C angles (deg): Fe1-C21-C22 = 149 (2), Ru5-C22-C21 = 175 (2), Fe2-C23-C24 = 150 (2), Ru6-C24-C23 = 166 (2). The PSEP theory[9] predicts that **3** is a coordinatively saturated species with 124 cluster valence electrons, when the $\mu_6\text{-}C_2$ ligand is counted as an 8e donor.

The striking spectroscopic feature of **2** and **3** is the unusual shielding of their C_2 signals when compared with the $\delta(C_\alpha)$'s of μ-vinylidene complexes [$M_2(\mu\text{-}C{=}CR_2)$: δ >230][8] and μ_3-alkylidyne complexes [$M_3(\mu_3\text{-}CR)$: δ >200][10] containing their partial structures. Such anomalous properties also may come from the strained structures.

Finally, **3** turned out to be one of the thermodynamically stable species in the reaction system as summarized in Scheme I. Although (i) simple thermolysis of **2** gave unidentified products, (ii) **3** was formed on treatment of **2** with $Ru_3(CO)_{12}$. In addition, (iii) formal dimerization of the $(\mu\text{-}C_2)(Cp^*Fe)Ru_3$ core in **4** leading to **3** was observed.

In marked contrast to the chemistry of C1 species, which has been studied extensively in relation to the CO reduction step of catalytic CO hydrogenation, the properties of the C2 species ($C_2H_xO_y$) that are formed after the first C-C coupling process have remained far less explored. This work reveals the utility of $MC{\equiv}CM$ as a versatile starting compound for *C2 chemistry*, in particular, *dicarbide* complexes. Thus the sequential transformation of **1** (permetalated ethyne) into permetalated ethene and ethane [$MC{\equiv}CM$ (**1**) → $M_2C{=}CM_2$ (**2**) → M_3CCM_3 (**3**)] has been realized by formal stepwise addition of dimetallic fragments to the C≡C bond in **1**.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters and bond lengths and angles and ORTEP drawings with anisotropic thermal ellipsoids and atomic numbering schemes for **2** and **3** (29 pages); tables of observed and calculated structure factors for **2** and **3** (41 pages). Ordering information is given on any current masthead page.

(4) A benzene solution (30 mL) of **1** (803 mg, 1.69 mmol) and $Ru_3(CO)_{12}$ (803 mg, 1.26 mmol) was refluxed for 9 h. After removal of $Ru_3(CO)_{12}$ and Fp^*_2 by repeated recrystallization, **2** (192 mg, 0.22 mmol, 13% yield) was isolated by recrystallization from CH_2Cl_2. Preparative TLC of the mother liquor (on alumina, developed with CH_2Cl_2-hexanes = 1:3) afforded **3** (82 mg, 0.05 mmol, 6% yield). **2**: ^{1}H-NMR ($CDCl_3$) δ 1.55 (s, Cp*); ^{13}C-NMR ($CDCl_3$) δ 9.5 (q, J = 128 Hz, C_5Me_5), 98.0 (s, C_5Me_5), 177.2 (s, μ_4-C_2), 191.1, 196.4, 205.6, 217.8 (s, CO), 262.5 (s, μ-CO); IR (KBr) 2082, 1997, 1981, 1963, 1953, 1775 cm^{-1}. **3**: ^{1}H-NMR ($CDCl_3$) δ 1.62 (s, Cp*); ^{13}C-NMR ($CDCl_3$) δ 9.2 (q, J = 129 Hz, C_5Me_5), 22.7, 31.6 (s, μ_6-C_2), 98.4 (s, C_5Me_5), 190.5, 190.7, 193.9, 202.8, 208.5, 210.4 (s, CO), 243.4 (s, μ-CO); the simple spectra obtained at room temperature may be explained in terms of local scrambling of the three CO's attached to Ru2; IR (KBr) 2068, 2047, 1997, 1825 cm^{-1}. Crystal data for **2**: $C_{32}H_{30}O_{10}Fe_2Ru_2$, M = 888.42, monoclinic, space group $C2/c$, a = 14.124 (6) Å, b = 11.537 (5) Å, c = 20.142 (5) Å, β = 93.23 (4)°, V = 3277 (4) Å^3, Z = 4, d = 1.80 g·cm^{-3}, μ = 18.09, R (R_w) = 0.0591 (0.0498) for 2668 data with $F > 3\sigma(F)$. Crystal data for **3**: $C_{41}H_{30}O_{17}Fe_2Ru_6$, M = 1512.79, triclinic, space group $P\bar{1}$, a = 16.801 (6) Å, b = 21.402 (8) Å, c = 14.436 (9) Å, α = 101.60 (4)°, β = 93.45 (4)°, γ = 93.50 (3)°, V = 5061 (4) Å^3, Z = 4, d = 1.99 g·cm^{-3}, μ = 23.28, R (R_w) = 0.0780 (0.1119) for 9217 data with $F > 3\sigma(F)$. The structure was solved by using the TEXSAN structure-solving system. A unit cell of **3** contained two independent molecules with essentially the same structure.

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Insertion of Phosphorus into the C-C Bond of Benzene As Observed by Collision-Mass Spectrometry

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The interaction of diverse atomic ions (or neutrals) with neutral (or ionized) benzene has been extensively examined in several studies.[1] There has been, however, no report to date for the phosphorus-benzene case. The results here presented provide evidence of ion-molecule reactions leading to the insertion of a phosphorus atom into the C-C bond of the aromatic ring.

For the generation of the ions $[P,C_6,H_6]^+$ of interest, benzene and PI_3 were reacted in the chemical ionization (CI) source[2] of a modified VG-ZAB tandem mass spectrometer of BEBE configuration.[3] The cations (m/z = 109) were selected under double-focusing conditions using B(1)E(1) and subjected to collisional activation (CA)[4] and neutralization-reionization (NR)[5] experiments. Phenylphosphine, in turn, was used to generate $C_6H_5PH^-$ by deprotonation with $O^{\bullet-}$ under similar CI conditions (abstraction of ring protons by $O^{\bullet-}$ can be excluded on thermo-

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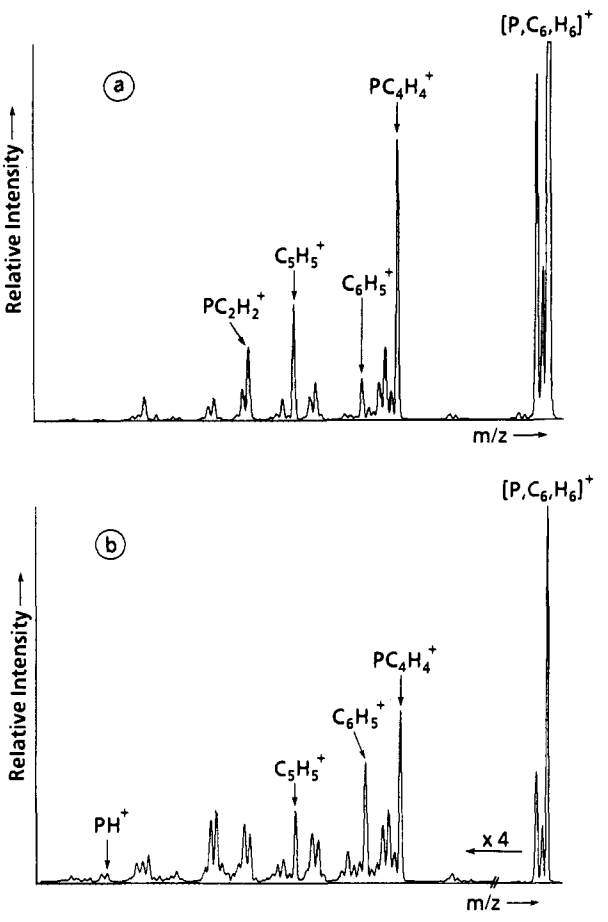


Figure 1. (a) CA spectrum of $[P,C_6,H_6]^+$ generated from PI_3 and benzene (helium, 80% transmission (T)); (b) CR spectrum of $[P,C_6,H_6]^+$ from deprotonated phenylphosphine (oxygen, 80% T).

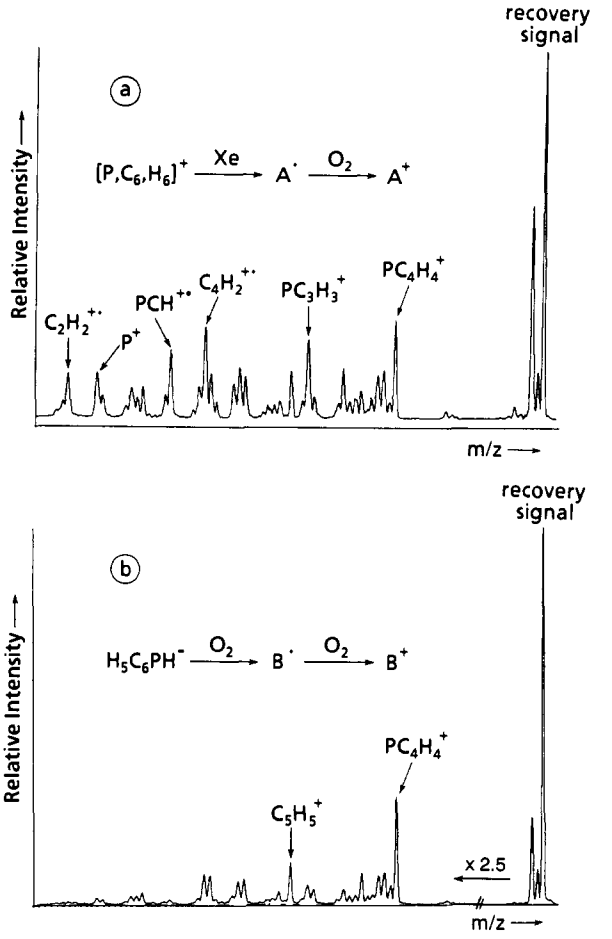
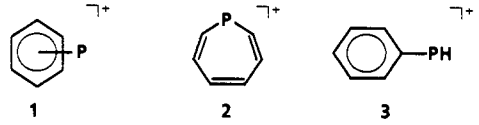


Figure 2. (a) NR spectrum (xenon, 80% T//oxygen, 80% T) of $[P,C_6,H_6]^+$ from PI_3 and benzene; (b) NR spectrum (oxygen, 80% T// oxygen, 80% T) of deprotonated phenylphosphine.

chemical grounds[6]). This anion, exempt of rearrangement processes,[7] was submitted to charge reversal (CR)[8] and NR experiments. Respectively, the set of ions $[P,C_6,H_6]^+$ formed by these alternative routes will be referred to as A^+ and B^+.

The clear differences between the spectra of Figure 1 rule out a single identity for A^+ and B^+, i.e., the major (if not only) component arising from the phosphorus–benzene reaction is not a C–H insertion product $HPC_6H_5^+$ (the expected main outcome from deprotonation and charge permutation on starting from phenylphosphine). The possibility of a simple long-lived phosphorus–benzene π-complex (**1**) is excluded from the absence of any intact $C_6H_6^{\cdot+}$ or loss of C_6H_6 to give P^+.[9] Insertion of phosphorus must then be occurring into a C–C bond of benzene to generate a cyclic species that preferentially eliminates the vicinal units PCH or HCCH. The isolobal analogy P ⟷ CH allows the correspondence of this insertion product with a phosphatropylium structure (**2**), while $HPC_6H_5^+$ is the phosphabenzylium isomer (**3**) from C–H insertion.



1 2 3

Nonetheless, as illustrated by the common features in the CA and CR spectra, it is clear that we are not dealing with "pure" species but with mixtures showing a preferential population of one of the two isomers. Noticeable are the cases of $m/z = 77$ in Figure 1a, revealing partial loss of PH from a phosphabenzylium component to give $C_6H_5^+$, and $m/z = 83$ in Figure 1b, resulting from a loss of C_2H_2 that, most likely, involves a phosphatropylium intermediate.[10] Thus, A^+ should consist principally, but not exclusively, of the phosphatropylium ion **2**, while B^+ would be made up mainly of the phosphabenzylium isomer **3**.[11] This CA behavior parallels that of the gas-phase ion chemistry of tropylium and benzylium ions, which is well-established through several exhaustive investigations.[12]

The significant loss of C_2H_2 from A^+ in Figure 1a is in line with the results of work on phosphacyclic and phosphaaromatic systems.[13] In fact, the main fragmentations for cation and radical cation derivatives from phosphaaromatics are the losses of neutrals

(6) The estimate is based on the ΔH_{acid} values for C_6H_6, OH·, and PH_3 taken from Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *1*, Suppl. No. 1.

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(9) (a) $C_6H_6^{\cdot+}$ and extensive loss of C_6H_6 were observed in the CA spectrum of the Fe–benzene$^+$ π-complex. See ref 1d. (b) On the basis of the ionization energies of C_6H_6 (9.25 eV) and P (10.49 eV), a π-complex **1** is expected to preferentially decompose to $C_6H_6^{\cdot+}$ and P; this is not observed experimentally.

(10) Interestingly, CA experiments on mass-selected $[P,C_4,H_4]^+$ (m/z = 83) generated from the ion populations A^+ and B^+, respectively, yield identical spectra. Loss of C_2H_2 may provide a thermodynamic sink along the fragmentation pathway of any phosphatropylium present, leading to $PC_4H_4^+$ in its most stable spiro configuration reported in a theoretical study (cf. Böhm, M. C.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 443).

(11) Of course, the partial isomerization A ⇄ B can also occur in the course of collisional activation.

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C_2H_2 and PCH. In this regard, the NR spectra (Figure 2) are most informative for confirmation of the neutral losses from the CA or CR experiments: in the case of A^+, and not for B^+, the ions $C_2H_2^{\bullet+}$ and $PCH^{\bullet+}$ are present as reionized fragments. The marked intensity of the recovery signals provides complementary evidence of the existence of the corresponding phosphatropylium and phosphabenzyl radicals in $A^\bullet$ and $B^\bullet$. Furthermore, the different fragmentation patterns of Figure 2 vs Figure 1 are indicative of some extent of structural reorganization during the neutralization-reionization events. Consistently, $C_6H_6^{\bullet+}$ remains always absent, corroborating the nonoccurrence of any phosphorus-benzene π-adduct.

Further work is underway to address the evaluation of the relative stabilities of the phosphatropylium and phosphabenzylium structures as well as the accessibility to suitable precursors of "pure" isomers.[14,15]

(14) Following a reviewer's suggestion, atomic P^+ (generated by 70 eV electron impact ionization of PI_3) has been reacted with benzene in the low-pressure regime using our 7 T FTICR mass spectrometer (for a description and operation of the machine, see: Eller, K. Ph.D. Thesis, Technische Universität Berlin, D83, 1991). In addition to charge transfer (80%) to generate $C_6H_6^{\bullet+}$, ionic products were observed which are in keeping with the intermediate formation of a phosphatropylium ion 2: $PC_4H_4^+$ (2%), $C_5H_5^+$ (3%), $PC_2H_2^+$ (5%), $C_3H_3^+$ (3%). The $C_6H_5^+$ ion (7%) is due to hydride atom abstraction by P^+.

(15) Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is appreciated. We are grateful to Professor D. K. Bohme for helpful comments.

Analysis of Artificial Proteins by Matrix-Assisted Laser Desorption Mass Spectrometry

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The growing use of recombinant DNA methods for the preparation of artificial proteins has created a pressing need for techniques for the rapid analysis of macromolecular structure. We report herein the use of matrix-assisted laser desorption mass spectrometry[1,2] to determine the structure and purity of an artificial copolypeptide prepared as part of our ongoing investigation of the crystallization behavior of periodic proteins.[3,4] The mass spectra demonstrate that SDS polyacrylamide gel electrophoresis (SDS-PAGE) is insensitive to the presence of degraded fragments of the artificial protein and that molecular masses estimated by SDS-PAGE may be in error by more than 100%. Furthermore, accurate mass determination by matrix-assisted laser desorption mass spectrometry allowed the discovery of two previously undetected mutations in the DNA code for the protein.

A synthetic DNA was constructed by multimerizing oligonucleotide fragments encoding two copies of the repeated undecapeptide of the target protein **1**.[5] The multimers were cloned and isolated, and a fragment encoding 14 undecapeptide repeats was inserted into the expression vector pET3-b.[3,6] The recombinant plasmid was used to transform *Escherichia coli* strain BL21(DE3)pLysS. After fermentation, the artificial protein was purified via acid precipitation of contaminants followed by ethanol precipitation of the target copolypeptide.[3] Amino acid analysis confirmed the composition of purified **1**, and Coomassie Blue staining of SDS-PAGE gels[7] revealed no contaminating proteins—the product was observed to migrate as a single tight band. On the other hand, the molecular weight reported by SDS-PAGE was found to be 43 000, which is more than twice the expected 17 207. Anomalously slow migration in SDS-PAGE is not uncommon, particularly for acidic proteins,[8] and has been attributed to reduced binding of SDS.

ASMTGGQQMGRDPMFKYSRDPMG-
$[AGAGAGAGPEG]_{14}$ ARMHIRPGRYQLDPAAN-
KARKEAELAAATAEQ (**1**)

In order to resolve the apparent molecular weight discrepancy, the copolypeptide was analyzed by matrix-assisted laser desorption mass spectrometry.[1,2] A small amount (1-10 pmol) of the polypeptide was mixed with a 10^4-fold molar excess of 3,5-dimethoxy-4-hydroxy-*trans*-cinnamic acid in an aqueous 30% acetonitrile solution containing 0.1% trifluoroacetic acid. The mixture was placed inside a time-of-flight mass spectrometer and irradiated with a neodymium/YAG laser (355 nm, 10 ns pulse). The ions formed by each laser pulse were accelerated by a 30-kV potential into a 2-m evacuated tube and detected using a Lecroy TR8828D transient recorder. This technique allows the rapid analysis of protein samples as small as 1 pmol containing relatively high concentrations of non-proteinaceous material. More importantly, the matrix-induced ionization results in the production of only intact ions, so that the molecular weight is readily accessible with no requirement for elaborate interpretation of the mass spectrum.

The mass spectrum of **1** is shown in Figure 1a. Although the observed value of m/z, 17 264 ± 2, shows the electrophoretically determined mass to be grossly in error, the observed value remains significantly different from the predicted m/z of 17 208.[9] In order to determine the origin of the difference, the sequence of a 741 base pair DNA fragment containing the protein coding region of the expression plasmid was determined. This analysis revealed C → T transitions in codons 96 and 101, causing two alanine-to-valine substitutions in the expressed protein. The calculated m/z value of the protein with the altered repetitive sequence **2** is 17 264—the experimentally determined value. The source of the sequence errors is not clear; because the sequence of the oligonucleotide was verified prior to multimerization, mutations must have arisen in a subsequent culturing step. Other multimers of similar sequence have been isolated and shown to be free of defects.

$-[AGAGAGAGPEG]_6[AGAGAGVGPEG]-$
$[VGAGAGAGPEG][AGAGAGAGPEG]_6-$ (**2**)

Signals arising from low molecular weight polypeptides are also visible in the spectrum shown in Figure 1a. Analysis of these signals, expanded in Figure 1b, shows that the line at m/z 5730 corresponds to fragment **3**, which consists of the intact N-terminal sequence of **1** followed by four copies of the repeating undecapeptide. The calculated mass of the molecular ion derived from

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(9) All m/z values refer to the protonated form of the polypeptide, $(M + H)^+$.

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