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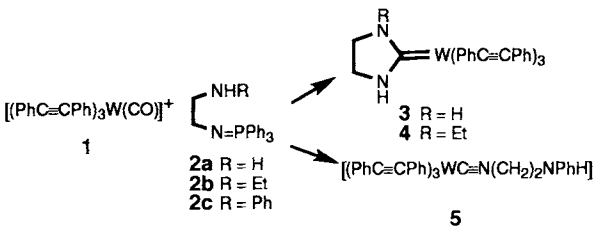
[19] We point out that the software for Bruker AMX spectrometers contains an error which may lead to mirror-image spectra and thus to erroneous signal assignments for X,Y correlations that employ the third frequency channel.
[20] **Note added in proof** (October 21, 1997): The detection of a $^{6}Li,^{15}N$ coupling (2 Hz) for the $[([^{6}Li]BuLi)_2\{[^{15}N](tmeda)_2\}]$ complex ($[D_8]$toluene, −110 °C) was recently reported: D. Waldmüller, B. J. Kotsatos, M. A. Nichols, P. G. Williard, *J. Am. Chem. Soc.* **1997**, *119*, 5479–5480.



The crystal structure of **3** confirms the presence of a carbene moiety. Figure 1 shows the molecular structure of **3**, the first tungsten complex that contains only carbene and alkyne ligands. Comparing the bond lengths and angles of **3** and **1** shows the coordination geometry at the metal center to be essentially unchanged.[7] Apparently, changing from a π-acidic carbonyl ligand to a nucleophilic carbene ligand[8] has little influence on the structure. The W–C7 bond length (2.167(8) Å) lies within the normal range for metal carbene complexes and is only slightly shorter than that reported by Dötz et al. for $[(CO)_4W{=}C(OMe)(o\text{-}C_6H_4C{\equiv}CPh)]$ [2.181(5)Å].[2a]

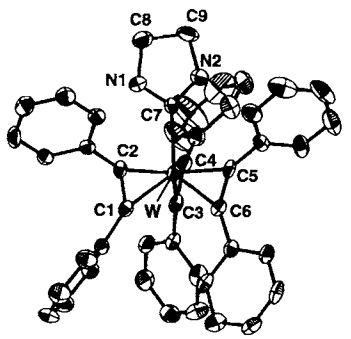


Figure 1. Molecular structure of **3** (numbering of aromatic carbon atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: W–C7 2.167(8), W–C1 2.049(9), W–C2 2.064(8), W–C3 2.062(9), W–C4 2.067(9), W–C5 2.098(8), W–C6 2.053(8), C1–C2 1.32(1), C3–C4 1.31(1), C5–C6 1.30(1); W-C7-N1 124.4(6), W-C7-N2 132.9(6).

Novel Alkyne Carbene Tungsten Complexes**

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Since the discovery of Fischer carbene complexes,[1a] numerous transition metal carbene complexes have been synthesized.[1] Among them, a few carbene complexes with coordinated alkyne ligands are known.[2–3] Such complexes are believed to be important intermediates for metal-mediated metathesis of alkynes.[2–4] Pioneering work by Dötz et al. has shown this reaction to be a versatile tool in organic synthesis.[4–5] All of these carbene complexes contain carbonyl ligands and transition metals in low oxidation states. We now report the synthesis of the first carbonyl-free alkyne carbene tungsten complexes **3** and **4**.

Treatment of **1** with an equimolar quantity of the amino-substituted iminophosphorane **2a** in dichloromethane gave the diaminocarbene complex **3** in 53% yield. The carbene group is presumably formed by deoxygenation of the carbonyl ligand by the iminophosphorane to give an isocyanide complex, which subsequently undergoes intramolecular attack by the amino group.[6] Complex **3** is stable in air and dissolves in most organic solvents. The ^{13}C NMR resonance of the carbene carbon atom at $\delta = 220.2$ is shifted downfield relative to that of $[(CO)_5W{=}C(NHCH_2)_2]$ ($\delta = 204.0$).[6]

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The *N*-ethyl compound **4** was prepared analogously from **1** and **2b**, but the phenyl-substituted iminophosphorane **2c** did not give the corresponding cyclic carbene species. Instead, the isocyanide complex **5** was obtained, presumably for steric reasons and because of the lower nucleophilicity of the aromatic amine. The substituents on the alkyne ligands also influenced the formation of carbene complexes. Neither $[(PhC{\equiv}CEt)_3W(CO)]$ nor $[(EtC{\equiv}CEt)_3W(CO)]$ reacted with **2a** to give the desired complex, and tungsten starting material was recovered. This illustrates the limitations of iminophosphorane in extracting the oxygen atom from coordinated carbonyl ligands.[6] Nevertheless, this approach provides another synthetic route to diaminocarbenes.[9]

Complex **3** catalyzes the polymerization of diphenylacetylene. In a typical experiment, a mixture of **3** (10 mol%) and PhC≡CPh in chlorobenzene was heated to reflux for 48 h. Polydiphenylacetylene was obtained as a yellow precipitate in 66% yield (based on the amount of diphenylacetylene consumed). The reaction solution contained pentaphenylbenzene (1.3%), pentaphenylcyclopentadiene (2.3%), and hexaphenylbenzene (3.7%). The benzene derivatives are the result of trimerization, while the pentaphenylcyclopentadiene

is believed to be formed in a manner similar to that reported by Green et al. for the reaction of $[(PhC{\equiv}CPh)_3W(NCMe)]$ with *o*-diphenylphosphanylstyrene.[10] Polydiphenylacetylene is a yellow solid, insoluble in most organic solvents, even boiling dichlorobenzene. It was characterized by solid-state ^{13}C NMR and mass spectrometry. The parent peak at $m/z = 3402$ corresponds to 19 diphenylacetylene units. The ^{13}C NMR spectrum shows signals at $\delta = 125$ and 144 for the aromatic and olefinic carbon atoms, respectively. Possible applications of this polydiphenylacetylene are currently being investigated.

Experimental Section

3: A solution of **1** [7] (300 mg, 0.4 mmol) and iminophosphorane **2a** (141 mg, 0.44 mmol) in dichloromethane (20 mL) was stirred at 25 °C for 16 h. The solvents were removed and the residue was chromatographed on silica gel (15 g) with dichloromethane/hexane (2/5, v/v) as eluent. The eluate was collected and concentrated to give **3** as a white solid. M.p. 178–180 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48-7.13$ (m, 30H, ArH), 6.50 (s, 2H, NH), 3.47(s, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 220.2$ (W=C), 198.9 (Ph*C*), 181.7 (Ph*C*), 143.9–125.5 (Ph), 45.8 (CH_2). Analysis: calcd for $C_{45}H_{36}N_2W$: C 68.53, H 4.60, N 3.55; found C 68.38, H 4.62, N 3.39.

Colorless single crystals of **3** were obtained by recrystallization from dichloromethane/hexane. Crystal data for **3**: $C_{45}H_{36}N_2W$, $M_r = 788.63$, orthorhombic, space group *Pbca*, $a = 20.589(5)$, $b = 20.463(6)$, $c = 16.503(6)$ Å, $V = 6953(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.507$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu = 34.246$ cm^{-1}, $F(000) = 3144$, $T = 298$ K, crystal dimensions $0.30 \times 0.35 \times 0.70$ mm. All measurements were performed on a Nonius CAD-4 diffractometer and refined by a least-squares treatment. $R_F = 0.039$, $R_w = 0.040$ for 3344 reflections with $I_0 > 2.0\sigma(I_0)$ and 434 variables. The NRCVAX program was used for the computation.[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100570. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code + (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

4: White solid, m.p. 182–183 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48-7.16$ (m, 30H), 3.81 (t, $^3J(H,H) = 9.3$ Hz, 2H), 3.26 (t, $^3J(H,H) = 9.3$ Hz, 2H), 2.27 (q, $^3J(H,H) = 7.4$ Hz, 2H), 0.03 (t, $^3J(H,H) = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 219.9$, 198.5, 181.6, 143.8–125.5 (Ph*C*), 47.4, 45.4, 43.2, 11.9; analysis: calcd for $C_{47}H_{40}N_2W$: C 69.12, H 4.94, N 3.43; found C 69.10, H 4.91, N 3.38.

5: White solid, m.p. 163–164 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.53-6.35$ (m, 35H), 4.07 (t, $^3J(H,H) = 5.3$ Hz, 2H), 3.43 (t, $^3J(H,H) = 5.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 193.7$, 177.9, 145.8, 142.2–112.8 (PhC), 44.2, 42.4; analysis: calcd for $C_{51}H_{40}N_2W$: C 70.84, H 4.66, N 3.24; found C 70.77, H 4.73, N 3.33.

Polydiphenylacetylene: Diphenylacetylene (225 mg) and **3** (100 mg, 0.126 mmol) in chlorobenzene were heated to reflux for 48 h. A yellow precipatate (149 mg, 66%) was collected by centrifugation with recovery of starting material (108 mg). ^{13}C NMR (solid state, 75 MHz): $\delta = 144$, 125; IR (KBr) $\tilde{\nu} = 1598$, 1578, 1492, 1441 cm^{-1}; MS (DCI): m/z 3402 ($[M+NH_4]^+$), 3224 ($[M+NH_4-178]^+$), 3046 ($[M+NH_4-2\times178]^+$), etc.

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A Convergent Synthesis of (+)-Parviflorin, (+)-Squamocin K, and (+)-5*S*-Hydroxyparviflorin**

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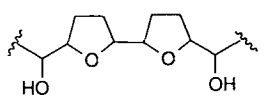
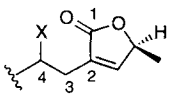
The diverse bioactivities of the annonaceous acetogenins as antitumor, immunosuppressive, pesticidal, antiprotozoal, anthelmintic, and antimicrobial agents have resulted in considerable attention being focused upon them.[1,2] The acetogenins almost invariably have the butenolide fragment **A** as a head group. Frequently, the most biologically active ones possess a hydroxyl group at C-4 of **A** and a dihydroxy bis(tetrahydrofuran) unit **B** somewhere in the chain.



B



A

Special interest accrues to those members that show remarkable differential cell cytotoxicity. For example, parviflorin (squamocin E, **1**)[3] shows ED_{50} values against human lung, breast, and colon carcinoma of 1.3×10^{-15}, 1.7, and 0.5 respectively. In trying to devise a convenient convergent general strategy to these bioactive acetogenins, we chose parviflorin as a target because of its partially hidden symmetry revealed by our retrosynthetic analysis outlined in Scheme 1. Regio- and diastereoselective introduction of the C-4 hydroxyl

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