metabolites of the new isolates established by chemical screening gives good evidence for further novel compounds. The screening of organisms from extreme biotopes previously not closely examined seems to be a successful approach to finding new potentially active metabolites.

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Phosphaalkyne Hydrometalation: Synthesis of $[RuCl(P{=}CH\,tBu)(CO)(PPh_3)_2]$**

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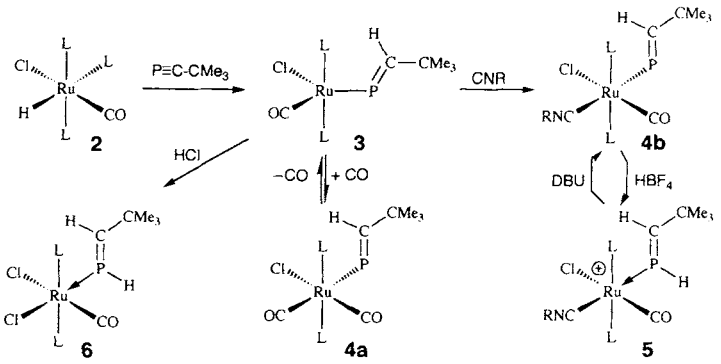
The notional similarity between alkynes (RC≡CR) and phosphaalkynes (P≡CR) raises the question of metal-mediated transformations of the reactive P≡C linkage.[1] To date, the majority of such studies have focused on oligomerizations, effected by organometallic substrates which bear essentially "innocent" co-ligands.[2, 3] We have previously described the interaction of P≡C*t*Bu (**1**) with a transition metal alkylidyne which proceeded by a metathesis of Mo≡C and P≡C triple bonds.[4] Subsequently it was shown that **1** could also be induced to couple with the metal–carbon multiple bonds in alkylidene[5] and vinylidene complexes.[6] Given that one of the most fundamental activation processes of alkynes by metal centers is the hydrometalation reaction to provide σ-vinyl complexes, it is noteworthy that the hydrometalation of **1** has remained prior to this report one of the "holy grails" of phosphaalkyne chemistry. Our studies on alkyne hydrometalation have centered on the complex $[RuHCl(CO)(PPh_3)_3]$ (**2**) and its derivatives,[7] and in this report we discuss the extension of this chemistry to **1**. This leads to the formation of stable coordinatively unsaturated σ-phosphaalkenyl complexes in a reaction completely and reassuringly analogous to those of alkynes. Furthermore such compounds are shown to be precursors to a range of complexes of otherwise unstable phosphaalkenes.

Treatment of a solution of **2** in dichloromethane with **1** leads to the clean formation of an orange-red complex, spectroscopic data (Table 1) for which are consistent with the formulation $[RuCl(P{=}CH\,tBu)(CO)(PPh_3)_2]$ (**3**) (Scheme 1). The ^{31}P NMR spectrum shows a doublet for the phosphane ligands (δ = 33.9, $^2J(P_2,P)$ 10.0 Hz) and a triplet (δ = 450.4, $^2J(P_2,P)$ 10.0 Hz) in an area considered typical of phosphaalkenyl ligands[6, 8] (although such a simple and non-kinetically stabilized derivative has not been previously reported). The alkenic proton appears as a doublet of triplets (δ = 7.12) with a large coupling ($^2J(P,H)$ = 16.9 Hz) to the adjacent phosphorus atom and a

Table 1. Selected spectroscopic data for the complexes $[Ru(P{=}CH\,tBu)Cl(CO)_n(PPh_3)_2]$; n = 1 (**3**) and 2 (**4a**).

	3	**4a**
IR (nujol [cm^{-1}]): ν(CO)	1929	2024, 1975
phosphaalkenyl		
NMR (CD_2Cl_2, 25 °C)		
$^{31}P\{^1H\}$: δRuPPh$_3$	33.9	22.1
δ(RuP=C)	450.4	369.5
$J(P_2,P)$ [a]	10.0	[b]
$^{13}C\{^1H\}$: δ(RuCO) [$J(P_2,C)$] [a]	202.4 [15.2]	198.7 [b], 193.0 [b]
δ(RuP=C) [J(P,C)] [a]	184.9 [58.9]	196.8 [62.5]
$\delta C(CH_3)_3$ [J(P,C)] [a]	40.8 [10.7]	41.8 [b]
$\delta C(CH_3)_3$ [J(P,C)] [a]	30.8 [14.3]	15.1 [b]
FAB-MS (nba matrix) [c]	940(64) [M^+ + nba]	940(41) [M^+ − CO + nba]
m/z (%) [assignment]:	791(9) [M − H$^+$]	819(18) [MH^+]
	–	789(2) [M^+ − H − CO]
	689(24)	689(24)
	[MH^+ − HPCH*t*Bu]	[MH^+ − HPCH*t*Bu − CO]

[a] Coupling in Hz. [b] Coupling not resolved. [c] nba = nitrobenzyl alcohol.



Scheme 1. Phosphaalkyne hydroruthenation. R = 2,6-$Me_2C_6H_3$; L = PPh_3.

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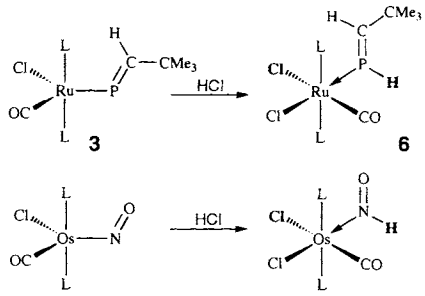
smaller coupling to the phosphorus atoms of the phosphane ligands ($^4J(P_2,H) = 2.8$ Hz). The gross molecular formulation is confirmed by FAB mass spectrometry; the mass spectrum shows in addition to a molecular ion, fragmentations for the loss of the phosphaalkenyl ligand as well as the formation of a nitrobenzyl alcohol adduct.

The recently reported transformation of a phosphaalkyne-(hydrido)iron complex to a fluoro(phosphaalkene) complex[9] is a process which could plausibly proceed by a hydroferration of the coordinated phospaalkyne, akin to the result reported here. Other than this report the remaining examples of phosphaalkenyl complexes are limited to those featuring kinetically stabilizing substituents[8a] or the metallacyclic complexes $[OsP{=}C(CF_3)O(CO)_2(PPh_3)_2]$[8b] and $[RhP{=}CtBuC(=CH_2)Cl(PiPr_3)_2]$.[6]

The implied coordinative unsaturation at ruthenium raises the questions of σ-π coordination of the phosphaalkenyl ligand and the possibility of ligand addition reactions. The former may be discounted as this would render the phosphane ligands diastereotopic, a possibility not supported by ^{31}P NMR data. The latter, however, provides a point of interest and this was subsequently investigated. The complex **3** rapidly reacts with CO under ambient conditions to provide the pale yellow complex **4a** (see Scheme 1), the stereochemistry of which follows unequivocally from spectroscopic data, whilst the gross molecular composition follows from FAB-MS data. Complex **4a** readily decarbonylates both in solution and in the solid state to reform **3**. This observation points to a substantial *trans* effect for the phosphalkenyl ligand, although this has not been previously appreciated since the majority of prior examples are of the "piano-stool" variety. A similar reaction occurs with 2,6-$Me_2C_6H_3NC$ to provide **4b**; however, in this case ligand addition is not as readily reversible. The phosphorus center in the free phosphalkyne **1** is typically electrophilic; however, hydroruthenation reverses this polarity making the phosphorus nucleophilic. This is reflected in the clean protonation of **4b** with $HBF_4 \cdot OEt_2$ to afford the cationic phosphaalkene complex **5**. The site of protonation is unambiguously established by the appearance of a doublet of triplets in the proton-coupled ^{31}P NMR spectrum at $\delta = 164.3$ ($J(P,P) = 45.0$, $J(P,H) = 376.4$ Hz), which collapses to a triplet in the proton-decoupled spectrum, and a doublet of doublet of triplets in the ^1H NMR spectrum at $\delta = 5.73$ ($^1J(P,H) = 375.8$; $^3J(H,H) = 20.5$ Hz; $^3J(P_2,H)$ discernable but not resolved) due to the phosphorus-bound proton. This protonation is readily reversed upon treatment with a non-nucleophilic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). These transformations in effect represent the unprecedented metal-mediated hydrogenation of a phosphaalkyne to a phosphaalkene.

The reaction of **3** with HCl also proceeds to a give a neutral phosphaalkene complex **6** (see Scheme 1). This raises questions about the bonding in **3** in that coordinative unsaturation in phosphaalkenyl complexes is normally accommodated by linearization of the M-P-C linkage, a process which renders the phosphorus center electrophilic. Clearly the phosphorus center in **3** is nucleophilic. Thus, we suggest the possibility that in metal centers that combine high d-occupancies and coordinative unsaturation the linearization of phosphaalkenyl ligands is not necessarily favored. In this context we note the isoelectronic relationship between the ligands -P=CR_2, -NO, and -NNR. The complex $[OsCl(NO)(CO)(PPh_3)_2]$ requires a linear nitrosyl on effective atomic number (EAN) grounds but actually features a bent and nucleophilic nitrosyl ligand as illustrated by the facile and reversible hydrochlorination to provide $[OsCl_2(HNO)(CO)(PPh_3)_2]$ (Scheme 2).[10] We therefore suggest



Scheme 2. Nitrosyl and phosphaalkenyl hydrochlorination. L = PPh_3.

that the arguments used to rationalize the geometries of late transition metal nitrosyl complexes[11] may equally well find application in the developing chemistry of phosphaalkenyl ligands.

Experimental Procedure

3: A solution of $[RuHCl(CO)(PPh_3)_3]$ (1.00 g, 1.05 mmol) in dichloromethane (50 mL) was treated with P≡C*t*Bu (0.43 mL, about 2.4 equivalents) and stirred for 1 h and then freed of volatiles. The residue was recrystallized (CH_2Cl_2/Et_2O) to provide **3**. Yield 0.76 g (92%). Anal. found C 62.5, H 6.2%. $C_{42}H_{40}ClOP_3Ru$ requires C 63.8, H 5.1%.

Note: The hydrometalation of adamantylphosphaalkyne proceeds under analogous conditions to those described above; however, the product could not be isolated in greater than about 90% purity due to its high solubility.

4a: Carbon monoxide was passed through a solution of **3** (0.15 g, 0.19 mmol) in dichloromethane (4 mL) for 2 min. Addition of diethyl ether (20 mL) and cooling to −10 °C for 12 h provided **4a**. Yield 0.13 g (84%). Analytical data not obtained due to rapid decarbonylation in the solid state.

4b: A solution of **3** (0.15 g, 0.19 mmol) in dichloromethane (5 mL) was treated with 2,6-$Me_2C_6H_3NC$ (0.03 g, 0.23 mmol) and stirred for 5 min and then freed of volatiles. The residue was crystallized from a mixture of dichloromethane and diethyl ether to provide **4b**. Yield 0.12 g (69%). Anal. found C 65.0, H 5.7, N 1.5%. $C_{51}H_{49}ClONP_3Ru \cdot 0.5CH_2Cl_2$ requires C 65.3, H 5.3, N 1.5%.

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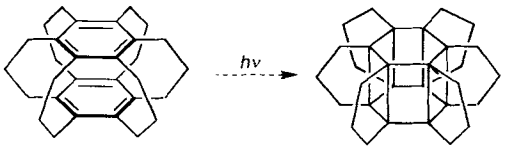
Synthesis of a "Molecular Pinwheel": [3.3.3.3.3.3]Cyclophane**

Youichi Sakamoto, Naomi Miyoshi, and Teruo Shinmyozu*

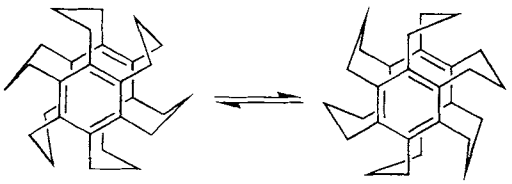
[3_6](1,2,3,4,5,6)Cyclophane **1**, a compound we have long sought[1, 2] and one of the final target molecules in the field of [3.3]cyclophane chemistry, has finally been synthesized and characterized. We expect **1** to have fascinating chemical and structural features. A photochemical isomerization of **1** to the propella[3_6]prismane **2** (Scheme 1) has been predicted based on



1 **2**

Scheme 1. Predicted photochemical isomerization of **1** to the propella[3_6]prismane **2**.

semiempirical MO calculations,[3] and a correlated inversion of the six trimethylene chains, which resemble six blades of a pinwheel, is expected in solution (Scheme 2).[4]



1a **1b**

Scheme 2. Predicted most stable conformations and correlated inversion of the six trimethylene bridges of **1**.

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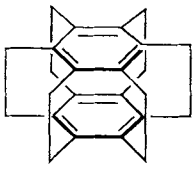
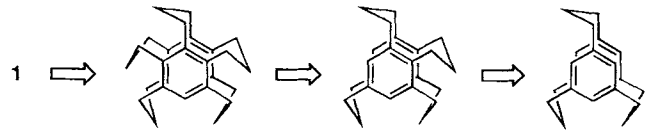
The synthesis of the highly strained [2_6](1,2,3,4,5,6)cyclophane **3**, named "superphane", was accomplished by Boekelheide et al. in 1979,[5] and the work opened the new field of superphane chemistry.[6] Since then syntheses, novel structures, and chemical properties of various superphanes such as **3** by Hopf et al.,[7] [4_5](1,2,3,4,5)ferrocenophane (superferrocenophane) by Hisatome et al.,[8] metal-capped [3_4](1,2,3,4)cyclobutadienophane by Gleiter et al.,[9] and [2_4](2,3,4,5)thiopenophane (superthiophenophane) by Tashiro et al.[10] have been reported.



3

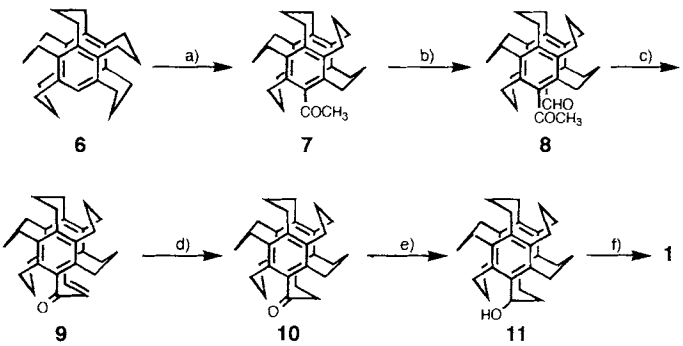
In our efforts toward the stepwise synthesis of **1** starting from the [3_3](1,3,5)cyclophane **4**[4c] (Scheme 3), we reported



1 **6** **5** **4**

Scheme 3. The stepwise synthetic approach.

the syntheses of the [3_4](1,2,3,5)cyclophane **5**[1] and the [3_5](1,2,3,4,5)cyclophane **6**,[2] in which the key reaction for the construction of a trimethylene bridge was the acid-catalyzed condensation between the acetyl group and the pseudogeminally substituted chloromethyl group. Recently we developed an alternative method using aldol condensation between the acetyl group and a pseudogeminally substituted formyl group, in place of chloromethyl group. This reaction proceeds in very high yields, and the resultant enones can be readily reduced to give trimethylene bridges. Since the precursors of **1** are now available in multigram quantities, we set about the synthesis of **1** from the [3_5]cyclophane **6** (Scheme 4).[2]



6 **7** **8** **9** **10** **11**

Scheme 4. Synthetic route to **1** from **6**. a) $(CH_3CO)_2O$, $AlCl_3$, CS_2, reflux, 3 d, **7**: 52% (based on recovered **6**); b) CH_3OCHCl_2, $AlCl_3$, CH_2Cl_2, room temperature (RT), 3 h, **8**: quantitative; c) 3N aqueous NaOH, THF, CH_3OH, reflux, 82 h, **9**: 92% (based on recovered **8**); d) H_2, PtO_2, $CHCl_3$-CH_3OH, RT, 41 h, **10**: quantitative; e) SmI_2, 1N aqueous KOH, THF, RT, 30 min; f) $AlCl_3$, $LiAlH_4$, THF, reflux, 12 h, **1**: 61% (based on **10**).

Formylation of the acetyl compound **7**, prepared by treatment of **6** with acetic anhydride in the presence of $AlCl_3$ (52%), quantitatively provided the pseudogeminally substituted compound **8**. Intramolecular aldol condensation of **8** under alkaline conditions afforded the enone **9** (92%), which was readily hydrogenated in the presence of catalytic amounts of PtO_2 to give the ketone **10** quantitatively. We initially attempted to reduce

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