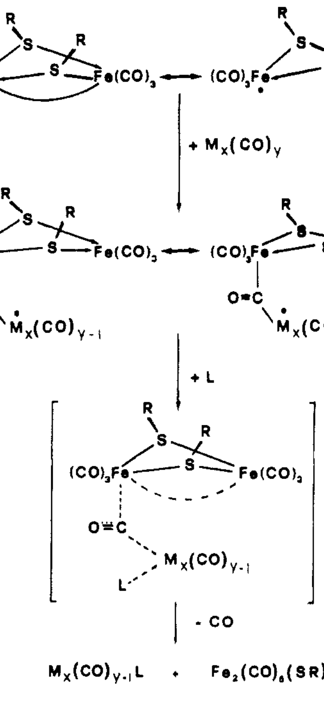
Table I. Experimental Data for the Reaction between Metal Carbonyl Complexes and Lewis Bases in the Presence of Iron Dimers as Catalyst[a]

				$[Fe(CO)_2(PPh_3)SMe]_2$			$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$			thermal route		
cluster	ligand	molar ratio	product	time, h	T, °C	% yield	time, h	T, °C	% yield	time, h	T, °C	% yield
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	PPh_3	1:1	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$	0.5	111	80	1.75	111	65[b]	18	80	33.7[e]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	PPh_3	1:1	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$	3	80	90						
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	$CNCH_2Ph$	1:1	$(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_2Ph)I$	0.75	45	70	0.75	45	90[b]	3	162	89[f]
$Mn_2(CO)_{10}$	PPh_3	1:2	$Mn_2(CO)_8(PPh_3)_2$	0.75	111	90	1.5	111	80[c]	7	111	90[g]
$Mo(CO)_6$	PPh_3	1:2	$Mo(CO)_4(PPh_3)_2$	3	80	90	no	cat.	*b*		150–185	*h*
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	$P(OEt)_3$	1:1.5	$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OEt)_3$	3	80	85				13	80	*i*
$Fe(CO)_5$	PPh_3	1:1	$Fe(CO)_4PPh_3$	3	80	80	5	111	90[c]	3	110	3.5[j]
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:1	$[Fe_3(CO)_{11}\{P(OEt)_3\}]$	15	25	80	15	25	60[d]	3–6	50	17[k]
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:2	$[Fe_3(CO)_{10}\{P(OEt)_3\}_2]$	15	25	90	15	25	70[d]	3–6	50	25[k]
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:3	$[Fe_3(CO)_9\{P(OEt)_3\}_3]$	3.5	40	75	3.5	40	40[d]	3–6	50	12[k]
$Ru_3(CO)_{12}$	$P(OMe)_3$	1:3	$[Ru_3(CO)_9\{P(OMe)_3\}_3]$	1.5	45	85	3	45	85[d]	1–3	67	7[l]

[a] All the reactions were carried out in cyclohexane, except those ones brought about at 111 °C which required toluene at the reflux, under N_2 flux, at the daylight. The reagent/catalyst molar ratio was 10:1. Typical runs involved 300 mg of carbonyl substrate dissolved in 150 mL of the appropriate solvent. All the compounds have been characterized by IR and ^1H and ^{31}P NMR spectra. [b] Reference 4a. [c] Reference 4b. [d] This work. [e] Treichel, P. M.; Shubkin, R. L.; Barnett, K. W. and Reichard, D. *Inorg. Chem.* **1966**, *5*, 1178. [f] Joshi, K. K.; Pauson, P. L.; Stubbs, W. H. *J. Organomet. Chem.* **1963**, *1*, 51. [g] Osborn, A. G.; Stiddard, M. B. H. *J. Chem. Soc.* **1964**, 634. [h] Dobson, G. R.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 1. [i] Haines, R. J.; Du Preez, A. L. *Inorg. Chem.* **1969**, *8*, 1459. [j] Cotton, F. A.; Parish, R. V. *J. Chem. Soc.* **1960**, 1440. [k] Grant, S. M.; Manning, A. R. *Inorg. Chim. Acta* **1978**, *31*, 41. [l] Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* **1972**, 2094.

Scheme I



formation of a 17-electron metal center which is well-known to undergo facile ligand substitution[8] by an associative S_N2 mechanism. The increased activity observed for the PPh_3-substituted derivatives can be accounted in terms of the steric hindrance of the bulky PPh_3 ligand which favors the flattening of the Fe_2S_2 tetrahedron with consequent weakening of the "bent" Fe–Fe bond. Finally, further insight into the operating mechanism has been gained by recording the ^{13}C NMR spectrum of the solution in which the reaction between $Ru_3(CO)_{12}$ (~40% ^{13}CO enriched) and $P(OMe)_3$ is taking place. As the reaction progresses, ^{13}CO displacement can be easily followed whereas almost no ^{13}CO incorporation into the catalyst is detected.

Acknowledgment. We thank Johnson-Mathey Ltd. for a loan of $RuCl_3$ and M.P.I. for support.

Registry No. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$, 12099-18-2; $(\eta^5\text{-}C_5H_5)Fe(CO)(CNCH_2Ph)I$, 51567-84-1; $Mn_2(CO)_8(PPh_3)_2$, 15279-67-1; $Mo(CO)_4(PPh_3)_2$, 15096-70-5; $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OEt)_3$, 33057-34-0; $Fe(CO)_4PPh_3$, 35679-07-3; $[Fe_3(CO)_{11}\{P(OEt)_3\}]$, 69092-12-2; $[Fe_3(CO)_{10}\{P(OEt)_3\}_2]$, 69092-23-5; $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, 12078-28-3; $Mn_2(CO)_{10}$, 10170-69-1; $Mo(CO)_6$, 13939-06-5; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8; $Ru_3(CO)_{12}$, 15243-33-1; PPh_3, 603-35-0; $CNCH_2Ph$, 10340-91-7; $P(OEt)_3$, 122-52-1; $P(OMe)_3$, 121-45-9; $[Ru_3(CO)_9\{P(OMe)_3\}_3]$, 38686-18-9; $[Fe(CO)_2(PPh_3)SMe]_2$, 63162-59-4; $Fe_2(CO)_6(SMe)_2$, 14878-96-7; $[Fe_3(CO)_9\{P(OMe)_3\}_3]$, 96095-77-1.

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[8] (a) Fox, A.; Malito, J.; Poe, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (b) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (c) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

Preparation, Structure, and Reactivity of an Anionic Ruthenium Ketenylidene: $[PPN]_2[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]$

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Summary: The new ketenylidene $[Ru_3(CO)_9CCO]^{2-}$ was prepared and fully characterized. The reaction with $CH_3OSO_2CF_3$ and H^+ leads to attack at the CCO and the metal framework, respectively. Reaction with $Fe_2(CO)_9$ yields $[FeRu_3(CO)_{12}(C)]^{2-}$.

Recent discoveries have revealed the diverse chemistry of metal cluster ketenylidenes and related compounds with respect to C–O activation, cluster building, and carbon–carbon bond formation.[1-3] The origin of this varied

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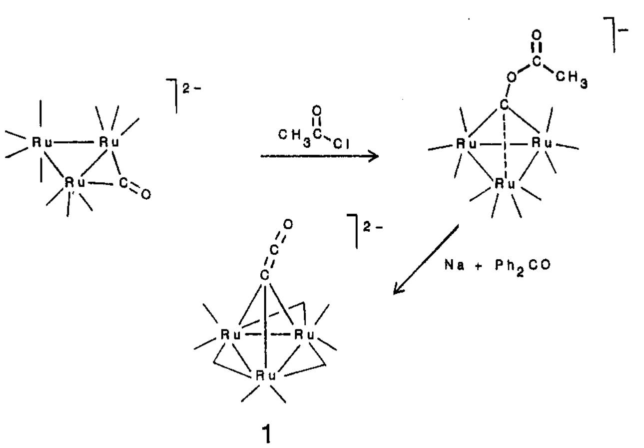
[1] Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G.R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214.

Scheme I



chemistry lies in the unique ability of the CCO ligand to act as either an electrophile, a nucleophile, or a carbide precursor. The reactivity and structural disposition of the CCO ligand of the trinuclear ketenylidenes varies drastically depending on the charge and identity of the metals of the host cluster. For example, $[Fe_3(CO)_9CCO]^{2-}$ and $[Fe_2Co(CO)_9CCO]^-$ are attacked by electrophiles at the α-carbon of the CCO moiety,[3,4] whereas the neutral or cationic ketenylidenes such as $H_2Ru_3(CO)_9CCO$, $H_2Os_3(CO)_9CCO$, and $[Co_3(CO)_9CCO]^+$ are attacked at the β-carbon by nucleophiles.[1,5-7] In addition, the CCO ligand in the neutral ketenylidene $H_2Os_3(CO)_9CCO$ is nearly perpendicular with respect to the metal plane, but in the anionic ketenylidenes the CCO is significantly tilted toward one of the metals. The synthesis and characterization of $[Ru_3(CO)_9CCO]^{2-}$, 1, was undertaken to discern whether these differences in structure and reactivity arise from the charge on the ketenylidene or from the positions of the constituent metal atoms in the periodic table. We also thought that $[Ru_3(CO)_9CCO]^{2-}$ might be a versatile precursor for mixed-metal carbide clusters, as was found for $[Fe_3(CO)_9CCO]^{2-}$.[3]

By analogy to the convenient synthesis of $[Fe_3(CO)_9CCO]^{2-}$, 1 was prepared in ca. 53% yield by acylation of a bridging carbonyl of $[Ru_3(CO)_{11}]^{2-}$,[8] followed by reductive cleavage of the activated CO with sodium benzophenone ketyl solution in tetrahydrofuran[2] (Scheme I). The product was isolated as the PPN^+ salt (PPN = bis(triphenylphosphine)nitrogen(1+)) and was purified by recrystallization from dichloromethane/ether.[9] A similar procedure yields the osmium analogue $[Os_3(CO)_9CCO]^{2-}$, but this compound has not yet been characterized in detail.

The single-crystal X-ray structure of 1 at −100 °C was determined.[10] As shown in Figure 1, the CCO ligand in $[Ru_3(CO)_9CCO]^{2-}$ is linear within experimental error (C1–C2–O2 = 178.8 (8)°) and is tilted away from the perpendicular to the plane of the metal atoms toward the middle of the Ru1–Ru3 bond by 11.3 (8)°. The recently reported structure of $H_2Os_3(CO)_9CCO$ shows the CCO entity in this case to be perpendicular with respect to the plane of the metals.[5] This contrasts with the structures of $[Fe_3(CO)_9CCO]^{2-}$ and $[Fe_2Co(CO)_9CCO]^-$ in which the CCO ligands are shown to be significantly tipped toward one of the metal atoms (33.5° and 24°, respectively).[2,4] Therefore, the disposition of the CCO ligand in $[Ru_3(CO)_9CCO]^{2-}$ is intermediate between the anionic first-row and neutral third-row ketenylidenes. The ketenylidene carbon C1 has its shortest bond to Ru2, the metal away from which it is tilted. Unexpectedly three symmetrically bridging carbonyls are present in 1.

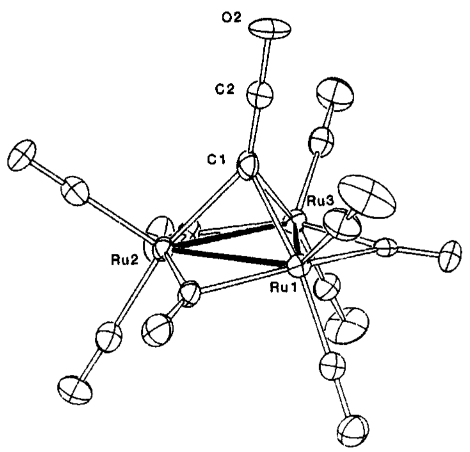
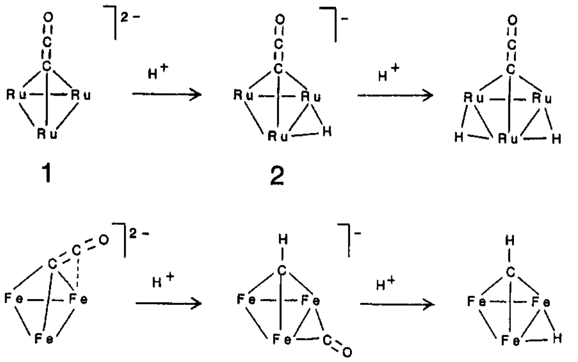


Figure 1. An ORTEP drawing of $[Ru_3(CO)_9(CCO)]^{2-}$, 1. The CCO ligand is slightly tilted toward the middle of bond Ru1–Ru3. Some selected bond distances and angles: Ru1–Ru2 = 2.747 (1), Ru1–Ru3 = 2.750 (1), Ru2–Ru3 = 2.792 (1), Ru2–C1 = 2.142 (7), Ru3–C1 = 2.169 (7), Ru1–C1 = 2.164 (8), C1–C2 = 1.300 (10), and C2–O2 = 1.171 (8) Å; average M–terminal CO carbon distance is 1.873 (12) Å; average M–bridging CO carbon distance is 2.113 (19) Å; C1–C2–C3 = 178.8 (8)°.

Scheme II



The infrared spectrum of 1 dissolved in dichloromethane contains four terminal CO stretching bands (2023 (m), 1982

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(2) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

(3) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158.

(4) Kolis, J. W.; Holt, E. M.; Hriljac, J. A.; Shriver, D. F. *Organometallics* **1984**, *3*, 496.

(5) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185.

(6) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1984**, *3*, 1322.

(7) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758.

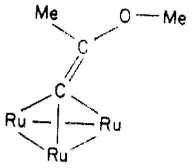
(8) $[PPN]_2[Ru_3(CO)_{11}]$ was synthesized by the method of: Bhattacharyya, A. A.; Nagel, C. C.; Shore, S. G. *Organometallics* **1983**, *2*, 1187.

(9) Anal. Calcd for $Ru_3C_{89}O_{10}P_4N_2H_{60}$: Ru, 18.13; C, 59.61; H, 3.62; N, 1.68. Found: Ru, 19.54; C, 59.47; H, 3.67; N, 1.64.

(10) Crystal data for $[PPN]_2[Ru_3(CO)_9(CCO)]$: a = 10.834 (1) Å, b = 13.029 (3) Å, c = 27.034 (5) Å, α = 96.57 (2)°, β = 97.29 (1)°, γ = 102.23 (1)°, V = 3659.8 (6) Å^3, space group $P\bar{1}$, Z = 2, d_{calcd} = 1.52 g/cm^3, μ = 7.45 cm^{-1}, Mo radiation, λ = 0.71073 Å, 13274 observed reflections; 7818 with $I \geq 3\sigma(I)$, ω–2θ scan mode, θ limits from 3 to 55°; Enraf-Nonius CAD-4 diffractometer. The ruthenium atoms were located on a Patterson map, and the other nonhydrogen atoms were found by difference Fourier techniques. The full-matrix-least squares refinement included anisotropic thermal parameters on all atoms in the cluster and isotropic on all PPN atoms. Phenyl hydrogens were included in structure factor calculations but were not refined: R_F = 0.053 and R_{WF} = 0.057. All calculations were performed on a Digital Equipment Corp. VAX 11/730 using Enraf-Nonius SDP program library and the Molecular Structure Corp. TEXLS full-matrix least-squares program.

(s), 1952 (vs), and 1899 (m) cm^{-1}) and one characteristic of bridging CO (1750 (m) cm^{-1}). The spectrum of a solid sample in a Nujol mull is similar. The ^{13}C NMR spectrum of 1 in CD_2Cl_2 at −90 °C contains three sharp carbonyl resonances of equal intensity at 273.3, 204.0, and 202.3 ppm and two higher field resonances for the β- and α-carbons of the CCO at 159.1 and −28.3 ppm. The overall intensity pattern is 3:3:3:1:1. The ^{13}C NMR spectrum of a sample enriched to ca. 30% in ^{13}C at all carbons clearly shows the peaks at 159.1 and −28.3 ppm to have superimposed doublets (J_{CC} = 96 Hz). The spectral data are consistent with the structure of the compound in the solid state.

Protonation of **1** with one equivalent of fluorosulfonic acid at −35 °C yields compound **2** which displays a singlet at −17.51 ppm in the ^{1}H NMR, indicating that the first proton attaches to the metal framework instead of the α-carbon of CCO, as in the case of $[Fe_3(CO)_9CCO]^{2-}$ (Scheme II).[2] The infrared spectrum of **2** in diethyl ether shows that it contains no bridging carbonyls (ν_{CO} = 2069 (w), 2032 (s), 2017 (m), 1999 (vs), 1969 (m), and 1927 (w) cm^{-1}). Addition of a second equivalent of acid gives the previously characterized[6] $H_2Ru_3(CO)_9CCO$, identified by its infrared, mass, and ^{1}H NMR spectra.[11] Therefore, protonation of **1** occurs exclusively on the metal framework. Reaction of **1** with the carbocation reagent $CH_3OSO_2CF_3$ leads to attack of the oxygen and the β-carbon of the CCO to give $Ru_3(CO)_{10}C{=}C(OMe)Me$, **3**, based on spectroscopic evidence[12] as well as a crystal structure determination.



3

The cationic ketenylidenes $[H_3Os_3(CO)_9CCO]^+$, $[H_3Ru_3(CO)_9CCO]^+$, and $[Co_3(CO)_9CCO]^+$ are susceptible to nucleophillic attack by methanol at the β-carbon of the CCO ligand.[1,5,7] In contrast, **1** is stable in methanol and no reaction is observed with excess methoxide ion.

As seen for $[Fe_3(CO)_9CCO]^{2-}$, the ruthenium ketenylidene also undergoes facile cluster building reactions. Hence reaction of **1** with $Fe_2(CO)_9$ yields a dianion, presumably $[Ru_3FeC(CO)_{12}]^{2-}$, which displays a characteristic carbide resonance in the ^{13}C NMR at 440.45 ppm downfield from Me_4Si. Protonation of this compound gives $H_2FeRu_3C(CO)_{12}$, identified by mass spectrum.[13]

In summary, the overall character of the anionic ketenylidene $[Ru_3(CO)_9CCO]^{2-}$, **1**, is that of a nucleophile. The CCO moiety of **1** is susceptible to attack by the carbocation reagent $CH_3SO_3CF_3$, although the site of attack is different than in $[Fe_3(CO)_9CCO]^{2-}$. Owing to the greater basicity of ruthenium over iron, **1** is protonated on the metal rather than the α-carbon as is observed for $[Fe_3(CO)_9(CCO)]^{2-}$. Unlike the previously reported neutral ruthenium and osmium ketenylidenes, **1** appears to have negligible electrophilic character at the β-C of the CCO. Additionally, compound **1** undergoes facile cluster building reactions, which should provide a convenient route to the synthesis of a wide range of mixed-metal carbide cluster compounds.

Acknowledgment. The research was supported by the NSF. The mass spectroscopy analysis program MASPAN was kindly provided by M. Andrews and H. D. Kaesz, UCLA. M.J.S. was the recipient of an ARCO fellowship. M.J.S. thanks Joseph A. Hriljac for helpful discussions.

Registry No. **1**, 97150-45-3; **2**, 97150-46-4; **3**, 97150-47-5; $H_2Ru_3(CO)_9CCO$, 90990-76-4; $[Ru_3FeC(CO)_{12}][PPN]_2$, 97150-49-7; $Fe_2(CO)_9$, 15321-51-4; $[Ru_3(CO)_{10}(\mu^3\text{-}COCOCH_3)]PPN$, 97150-51-1; $[Ru_3(CO)_{10}(\mu\text{-}Co)][PPN]_2$, 97150-52-2; $[OS_3(CO)_9(CCO)]^{2-}$, 97150-53-3; CH_3COCl, 75-36-5.

Supplementary Material Available: Complete listings of positional and thermal parameters, bond angles, bond distances, and observed and calculated structure factors for $[Ru_3(CO)_9(CCO)][PPN]_2$ (112 pages). Ordering information is given on any current masthead page.

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[11] For $H_2Ru_3(CO)_9CCO$: ν_{CO} (pentane) 2120 (w), 2086 (m), 2061 (s), 2040 (mw), 2016 (m)cm^{-1}. A MASPAN analysis of the parent envelope centered at 599 mass units in the 15-EV electron-impact mass spectrum yields an agreement factor of R = 5.2% for $H_2Ru_3(CO)_{10}C$; ^{1}H NMR (CD_2Cl_2) −17.99 ppm relative to Me_4Si.

[12] For $Ru_3(CO)_{10}CC(OMe)Me$: ν_{CO} (pentane): 2093 (w), 2061 (vs), 2041 (s), 2024 (s), 2004 (m) (sh), 1918 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 3.81, 2.36 ppm relative to Me_4Si; ^{13}C NMR (CD_2Cl_2, $^-$90 °C) 263.0 (br), 195.6, 192.8 ($^1J_{CC}$ = 55 Hz), 168.7 ($^1J_{CC}$ = 55 Hz) ppm relative to Me_4Si; 70-eV EI mass spectrum, 655 mass units, successive loss of 10 CO's.

[13] For $H_2Ru_3FeC(CO)_{12}$: 70-eV EI mass spectrum shows parent ion envelope centered at 709 mass units and successive loss of 12 CO's.

Synthesis of 1-Phenylarsole and 1-Phenylstibole

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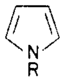
Received April 22, 1985

Summary: Hydrogenation of 1,4-diiodobuta-1,3-diyne with diimide gave 1(*Z*),4(*Z*)-diiodobuta-1,3-diene which on treatment with *n*-butyllithium followed by phenylarsenic dichloride or phenylantimony dichloride afforded 1-phenylarsole or 1-phenylstibole, respectively.

The pyrrole analogues **2–5** are of general interest for testing concepts of aromaticity.[1] While 1-phenylphosphole is available,[2,3] only more highly substituted derivatives of **3–5**[4-7] have been reported. Since the properties of the parent ring systems may be masked by substitution, a preparation of the C-unsubstituted heteroles **3–5** would be a valuable addition to the study of element–carbon conjugation. We now wish to report on a general synthesis which allows preparation of the 1-phenylheteroles of the group 5 elements.



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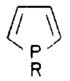

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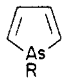

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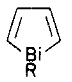

5

Since perphenylheteroles **7** have been prepared from the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (**6**)

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[1] For a critical discussion of phosphole aromaticity see: Quinn, L. D. "The Heterocyclic Chemistry of Phosphorus: Systems Based on the Phosphorus-Carbon Bond"; Wiley: New York, 1981; pp 406–414.

[2] Märkl, G.; Potthast, R. *Tetrahedron Lett.* **1968**, 1755.

[3] Mathey, F.; Mankowski-Favelier, R. *Org. Magn. Reson.* **1972**, *4*, 171.

[4] Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 5099. Braye, E. H.; Hübel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406.

[5] Märkl, G.; Hauptmann, H. *Tetrahedron Lett.* **1968**, 3257.

[6] Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95.

[7] Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495.

0276-7333/85/2304-1478$01.50/0