J_{PH} = 6.6, 9.9 Hz), 1.83 (6 H, m) and 0.51 (9 H, m) (bound PEt$_3$), 1.0 and 0.9 (inferred from decoupling experiments). ^{1}H NMR for IVb: δ –1 (broad). Resonances corresponding to fluorene and bifluorene were also observed.

In a similar procedure carried out in toluene-d_8, the reaction was continued for 6 days at 100 °C. In addition to the resonances observed for fluorene, bifluorene, IIIb, and IVb, the hydride resonance of Vb was also observed at δ –8.54 (t, J_{PH} = 31 Hz). Integrations indicated that the fluorene plus bifluorene observed accounted for greater than 95% of the initial I and that the hydride peak accounted for greater than 65% of I; at this point, some IVb was still present, and some decomposition was evident.

Isolation of (η^1-C$_{13}$H$_9$)Mn(CO)$_3$(PEt$_3$)$_2$. Typically, 0.25 g (2.1 mmol) of PEt$_3$ was added to a partially dissolved suspension of 100 mg (0.33 mmol) of I or VI in 2 mL of hexane. Reactions starting with I were carried out for approximately 24 h at 37 °C and those starting with VI for 45 min at room temperature. After the reaction was stopped, solvent and excess PEt$_3$ were pumped off, and the resulting product was recrystallized from hexane. Typical isolated yields for either method were 40–45%. All NMR data are for benzene-d_6. ^{1}H NMR (δ): six-membered-ring protons, 7.98 (2 H, d, 7.4 Hz), 7.96 (2 H, d, 7.5 Hz), 7.43 (2 H, t, 7.4 Hz), 7.31 (2 H, t, 7.3 Hz); five-membered-ring proton, 4.49 (1 H, dd, 6.8, 9.5 Hz); bound PEt$_3$ protons, 1.82 (6 H, m), 0.95 (15 H, overlapping multiplets), 0.54 (9 H, m). ^{13}C{^{1}H} NMR (δ): CO carbons, 223 (broad, weak, asymmetric); quaternary carbons, 158.5,

138.8; arene carbons, 124.6, 123.6, 122.1, 119.6; C(9), 28.3 (t, J_{PC} = 8.4 Hz); PEt$_3$ methylene carbons, 19.6 (d, J_{PC} = 21 Hz), 18.7 (d, J_{PC} = 21 Hz); PEt$_3$ methyl carbons, 7.3, 7.1. ^{31}P NMR (δ): 45.3, 40.5. IR: ν_{CO} (hexane) 2000 (w), 1917 (s), 1887 (m) cm^{-1}. Anal. Found (calcd) for C$_{28}$H$_{39}$MnO$_3$P$_2$: C, 62.0 (62.2); H, 7.34 (7.27).

Observation of IIIa. The reaction of I with PBu$_3$ was investigated briefly by NMR spectroscopy. These studies yielded observations similar to those with PEt$_3$, and only key results are indicated here. ^{1}H NMR (ca. 15% by volume PBu$_3$ in benzene-d_6): resonance for the five-membered-ring proton of IIIa at δ 4.49 (dd, J_{PH} = 9.4, 6.9 Hz); resonance for the hydride proton of Va at δ –8.49 (t, J_{PH} = 31 Hz).

In attempts to synthesize IIIa from VI by use of the method for IIIb described above, IR spectra of reaction mixtures indicated nearly quantitative conversion of VI to IIIa. However, when solvent was removed, the crude yellow oil, heavily contaminated by excess PBu$_3$, could not be purified by recrystallization. Column chromatography (elution with hexane on a Florisil column at –15 °C) and extraction with degassed, aqueous HCl led to products heavily contaminated by fluorene. IR: ν_{CO} (hexane) 1999 (w), 1915 (s), 1888 (m) cm^{-1}.

Closed-Structure Arsinidene Complexes of 16-Electron Cyclopentadienylruthenium Carbonyl Fragments. Molecular Structures of {[CpRu(CO)]$_2$(μ-CO)(μ-AsR)}, R = Me and Ph

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The reaction of the diphenylacetylene carbonyl-substitution product of [CpRu(CO)$_2$]$_2$, specifically, [Cp$_2$Ru$_2$(CO)$_2$(μ-CO)(PhCCPh)] (1) with the cyclopolyarsines *cyclo*-(AsMe)$_5$ and *cyclo*-(AsPh)$_6$ have afforded monoarsinidene (RAs) products by displacement of diphenylacetylene. These products are structurally related to the supposed structure of the cis isomer of [CpRu(CO)$_2$]$_2$ in which one μ-CO ligand has been replaced by a μ-AsR ligand to form {[CpRu(CO)]$_2$(μ-CO)(μ-AsR)}. The R = Me (2) and Ph (3) products obtained from 1 have been crystallographically characterized. Compound 2: orthorhombic, *Pnma*, *a* = 16.170 (4) Å, *b* = 14.658 (3) Å, *c* = 6.309 (1) Å, *V* = 1495.3 (6) Å^3, *Z* = 4, *R(F)* = 2.84%. Compound 3: monoclinic, *P2$_1$/c*, *a* = 8.241 (3) Å, *b* = 27.930 (10) Å, *c* = 7.925 (3) Å, β = 96.64 (3)°, *V* = 1811 (1) Å^3, *Z* = 4, *R(F)* = 3.02%. The geometry at the μ-arsinidene As atom in both structures is pyramidal, and both contain Ru–Ru bonds, whereas the overwhelming majority of known dinuclear μ-AsR structures display planar As-atom environments and are not metal–metal bonded. These structures represent the first dinuclear ruthenium–inidene structures for any of the group-15 elements and the first structural characterization of a closed-structure arsinidene complex.

Introduction

Transition-metal complexes of the "inidene" ligands, RE (E = P, As, or Sb), are known in a large variety of structural forms due to the ability of the ligand to adopt μ_2-, μ_3-, and μ_4-bridging modes. This structural adaptability has been productively used in the construction and stabilization of multinuclear complexes.[2-5]

For dinuclear complexes containing μ_2-RE ligands, two subclasses are known: type I containing 16-electron metal fragments and type II containing 15-electron metal fragments.[6a] Each of the types is further divisible into pairs

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(5) Isoelectronic cationic inidene complexes of group-16 elements are also known, e.g., [Cp(CO)$_2$Mn]$_2$SR$^+$, R = Ph[5a] and Et,[5b] and [Cp(CO)$_2$Mn]$_2$TePh2$^+$.[5c] (a) Braunwarth, H.; Huttner, G.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 698. (b) Burckett-St. Laurent, J. C. T. R.; Caira, M. R.; English, R. B.; Haines, R. J.; Nassimbeni, L. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1077. (c) Huttner, G.; Schuler, S.; Zsolani, L.; Gottlieb, M.; Braunwarth, Minelli, M. *J. Organomet. Chem.* **1985**, *286*, 317.

of valence tautomers, a and b. In the Ia and IIa structure
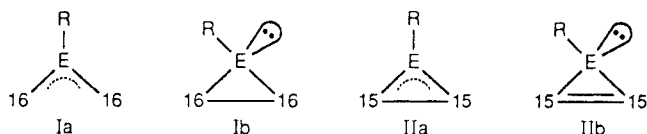
types (often referred to as "open" complexes), the stereochemistry at E is planar and E is best regarded as a four-electron donor. In the Ib and IIb "closed" structures, E is pyramidal and functions as a two-electron donor.[6b] Huttner has usefully compared the relationship of Ia and Ib to that of the isolobal valence isomers, the allyl and cyclopropyl anions.[4]

Crystallographically verified examples of all four types are known,[3] although only a single example of a Ib structure for a stibinidene complex has been confirmed, {Fe$_2$-(CO)$_8$[μ-SbCH(SiMe$_3$)$_2$]}.[8] On the basis of IR evidence only, [Co$_2$(CO)$_6$(μ-PPh)(μ-CO)] has been described as type Ib, structurally analogous to Co$_2$(CO)$_8$.[7]

Our study of the reactions of cyclopolyarsines, *cyclo*-(RAs)$_n$, with metal carbonyls has led us to examine their use as a potential source for the generation of arsinidene ligands.[9] This procedure offers advantages (e.g., high yields and no condensation byproducts) over more commonly used methods that employ REX$_2$ reagents (X = halogen or hydrogen) with metal carbonyl ions to form inidene complexes. We now report the results of a study of the reactions of *cyclo*-(AsPh)$_6$ and *cyclo*-(AsMe)$_5$ with the diphenylacetylene-substituted Ru complex 1, which
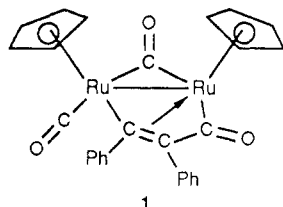

has led to the formation of two arsinidene complexes of the Ib type [(CpRuCO)$_2$(μ-CO)(μ-AsR)*Ru–Ru*], which have been crystallographically characterized. In addition to being rare examples of 16-electron "closed" inidene structures, these new complexes are, to our best knowledge, also the first examples of dinuclear ruthenium–inidene complexes of any kind.
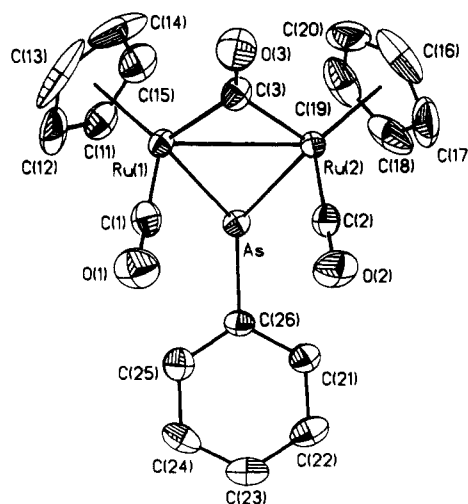
Results and Discussion

Synthesis of 2 and 3. A facile route to the preparation of dinuclear cyclopentadienylruthenium carbonyl com-
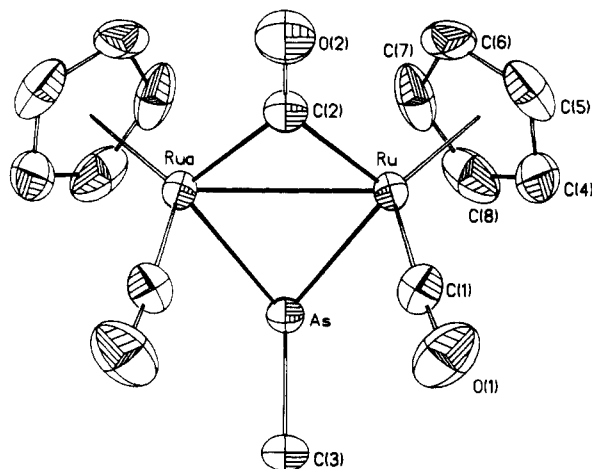
Figure 1. Molecular structure and labeling scheme for 2 drawn with 45% ellipsoids.
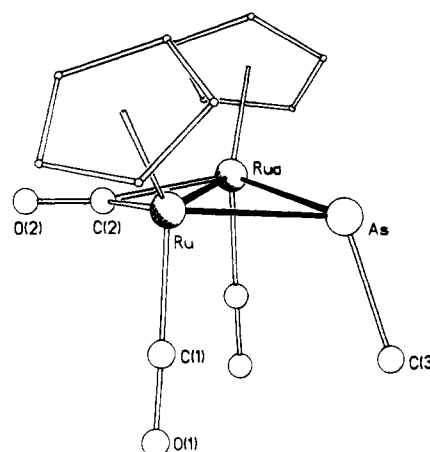
Figure 2. View of 2 emphasizing the pyramidal geometry at the As atom.

Figure 3. Molecular structure and labeling scheme for 3 drawn with 45% ellipsoids.

plexes can be found through the irradiation of [CpRu-(CO)$_2$]$_2$ with diphenylacetylene to form the metallacycle 1.[10] In the presence of another ligand (e.g., alkynes, alkenes, phosphites, diazoalkanes, etc.), in a refluxing toluene solution of 1, rapid, nearly quantitative exchange for the

(6) (a) A dinuclear complex with 14-electron fragments has been reported by Cowley and co-workers, {[CpV(CO)$_2$]$_2$[μ-PC$_6$H$_3$(t-Bu)$_3$]}, but a V–V distance of 2.924 (1) Å makes it uncertain if this is an open or closed structure.[3] (b) A third class, RE(17)$_2$, e.g., PhP[Co(CO)$_4$]$_2$,[7] is an example of a simple trivalent REX$_2$ compound and not an inidene complex.

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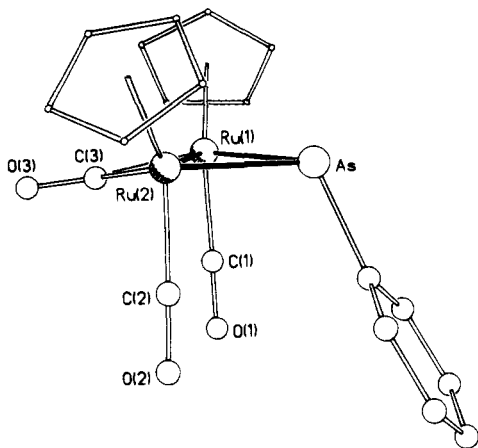
Figure 4. View of **3** emphasizing the pyramidal geometry at the As atom.

alkyne can occur.[11] Given this, we began a study of the use of cyclopolyarsines as diphenylacetylene-displacing agents. In the synthesis of **2** and **3**, compound **1** was refluxed in a toluene or xylene solution of $(RAs)_n$ (**2**, R = Me, n = 5; **3**, R = Ph, n = 6). In both instances, the response of the cyclopolyarsine to acetylene loss from **1** is the same: the dimetallacyclopentenone ring was replaced by a μ_2-bridging organoarsinidene. There is no evidence for formation of catenated arsinidene chains as has been found in mononuclear bis(cyclopentadienyl)titanium complexes (e.g., $Cp_2Ti(AsR)_3$)[12] or binuclear catenate complexes (e.g., $[CpMo(CO)_2]_2(AsMe)_5$).[9d] The same arsinidene products, **2** and **3**, cannot be prepared from the reaction of $[CpRu(CO)_2]_2$ and the cyclopolyarsines. Instead various decarbonylation products are obtained that will be the subject of a future publication.

Compounds **2** and **3** were identified by spectroscopic data, and their structures were confirmed by X-ray crystallography. Both products exhibited similar ν_{CO} stretching patterns with a band in the bridging region (1781–1801 cm^{-1}).

Molecular Structures of 2 and 3. The structures of **2** and **3** are shown in Figures 1–4. The structures may be regarded as derivatives of cis-$[CpRu(CO)(\mu\text{-}CO)]_2$ (which has never been isolated but is inferred from an analysis of the fluxional behavior of the trans isomer, **4**),[13] in which one of μ-CO ligands has been replaced by μ-RAs. The Cp–Ru–Ru–Cp torsion angle in both is 0.0°. The dihedral angle between the Ru_2As and Ru_2C planes of the central Ru_2AsC "butterfly" is 14.5 (1)° for **2** and 12.9 (1)° for **3** with the wings bent away from the Cp rings; in **4**, the Ru_2C_2 plane is rigorously planar.[14] The presence of the RAs ligand has caused an enlargement of the central framework compared to **4**. In **4**, the Ru–Ru distance is 2.735 (2) Å and increases to 2.788 (1) Å for **2** and 2.786 (1) Å for **3**; the average Ru–μ(CO) distance in **4** is 1.99 (1) Å and increases to 2.024 (5) Å for **2** and 2.051 (5) Å for **3**. The Ru–Ru distances are considerably longer than that found in cis-$\{[CpRu(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)(Ru\text{-}Ru)\}$, 2.707 (1) Å, reflecting the more effective donation of electron density

from a metal–metal π^* orbital into the $p\pi$ acceptor orbital of methylene.[11b]

The pyramidal As-atom stereochemistry is clearly evident in Figures 2 and 4. The angle of depression of the As–C bond from the Ru_2As plane is 64.1 (2)° for **2** and 63.6 (2)° for **3**. The Ru–As–C angles, 111.2 (2)° for **2** and (av) 111.5 (2)° for **3**, provide further support for pyramidal geometry.

The closed (type Ib) structures of **2** and **3** are the result of the incorporation of the arsinidene ligand in the stable $\{[CpRu(CO)]_2(\mu\text{-}CO)\}$ framework. The stability of this structure is evidenced by our inability to affect decarbonylation of **2** or **3** to produce a type IIa structure or to carbonylate **2** or **3** to form $RAs[CpRu(CO)_2]_2$. The presence of a second μ-ligand in these closed inidene complexes appears to provide the necessary stabilization, although recent evidence clearly suggests that the energy difference between open and closed forms is small.[5a] The only other previously confirmed closed 16-electron inidene complex, $[Fe_2\{\mu\text{-}SbCH(SiMe_3)_2\}(CO)_8]$,[8] contains a pyramidal RSb unit but is not stabilized by a second bridging ligand. Although this complex is isoelectronic with $Fe_2(CO)_9$, it has one μ-ligand whereas $Fe_2(CO)_9$ has three. Evidence was also found for the formation of an open isomer of the Fe_2Sb complex in reactions producing the closed complex, but the open isomer proved too unstable to isolate. The large $Si(Me)_3$ groups may provide steric reasons for the closing of the Fe–Sb–Fe angle, the pyramidal Sb atom, and the formation of an Fe–Fe bond (although, at 2.801 (1) Å it is rather long).

The pathway for the formation of **2** and **3** may involve the loss of diphenylacetylene on heating of **1** in aromatic solvent, leading to the formation of a reactive intermediate containing a Ru–Ru double bond, $Cp(CO)Ru{=}Ru(CO)$-$Cp(\mu\text{-}CO)]$, **5**. This unsaturated intermediate coordinates the cyclopolyarsine and promotes ring fragmentation. Precedent for the proposed formation of a Ru${=}$Ru bonded intermediate is the reported synthesis of isoelectronic $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}NO)]_2$, which on the basis of spectroscopic evidence is believed to contain a metal–metal double bond.[15] Evidence for the formation of **5** is found in the IR of the reaction as it progresses; after 15 min, a refluxing toluene solution containing **1** and the cyclopolyarsine displays a bridging carbonyl band (ν_{CO} = 1723 cm^{-1}) that later disappears completely.

The formation of a monoarsinidene complex rather than a catenated arsinidene chain such as is found for Cp_2Ti-$(AsR)_3$ and $[CpMo(CO)_2](AsR)_5$ likely results from the presence and stability of the bridging CO group in **5**, which prevents rotation of the bimetallic species about the Ru–Ru bond. If a two-electron-deficient intermediate was formed that would allow for rotation, more than one (RAs) unit could be coordinated as a catenated chain of organoarsines, and two-electron donors similar to the early transition metal–organoarsine clusters would be possible.

Experimental Section

General Procedure. Unless otherwise specified, all manipulations were carried out under an atmosphere of N_2. Melting points were measured on a Mel-Temp apparatus and were uncorrected. For **2**, infrared spectra were recorded on a Nicolet 50XB FTIR spectrophotometer as solutions in closed cells. ^1H NMR spectra were obtained on a Bruker 250-MHz spectrometer in deuterated solvents with TMS as an internal reference. For **3** infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer, and ^1H NMR spectra were recorded on a Varian FT 80 spectrometer. HPLC analysis of all compounds

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Table I. Crystallographic Data for
[(CpRu(CO))₂(μ-CO)(μ-AsR)]

	R = Me (2)	R = Ph (3)
formula	C₁₄H₁₃O₃AsRu₂	C₁₉H₁₅O₃AsRu₂
cryst syst	orthorhombic	monoclinic
space group	*Pnma*	*P2₁/c*
a, Å	16.170 (4)	8.241 (3)
b, Å	14.658 (3)	27.930 (10)
c, Å	6.309 (1)	7.925 (3)
β, deg	90	96.64 (3)
V, Å³	1495.3 (6)	1811 (1)
Z	4	4
D(calcd), g cm⁻³	2.249	2.085
μ(Mo Kα), cm⁻¹	41.78	34.60
T(max)/*T*(min)	1.44	1.36
color	orange	orange
size, mm	0.33 × 0.36 × 0.39	0.30 × 0.33 × 0.40
temp, °C	23	22
diffractometer	Nicolet R3m/μ	same
radiation	Mo Kα (λ = 0.710 73 Å)	same
monochromator	graphite	same
scan limits, deg	4 ≤ 2θ ≤ 52	4 ≤ 2θ ≤ 55
data collected	+*h*,+*k*,+*l*	±*h*,+*k*,+*l*
scan method	Wyckoff	Wyckoff
rflns coll	1726	4556
indpdnt rflns	1523	4164
R(int), %	NA	2.21
obsd rflns (*nσF*₀)	1308 (*n* = 5)	3222 (*n* = 5)
decay, %	<1	<1
R(*F*), %	2.84	3.02
R(w*F*), %	3.16	3.72
GOF	1.091	0.928
Δ/σ (final)	0.04	0.04
Δ(ρ), e Å⁻³	0.42	0.57
*N*₀/*N*ᵥ	13.4	14.2

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal
Parameters (Å² × 10³) for [(CpRu(CO))₂(μ-CO)(μ-AsMe)] (2)

	x	*y*	*z*	*U*ᵃ
Ru	903.0 (2)	8450.9 (2)	3273.5 (6)	32.9 (1)
As	70.8 (4)	7500	5688 (1)	37.8 (2)
C(1)	−19 (3)	8639 (4)	1591 (8)	47 (2)
C(2)	1315 (4)	7500	1200 (11)	39 (2)
C(3)	−1122 (4)	7500	4840 (17)	63 (3)
C(4)	1134 (4)	9857 (4)	4387 (17)	87 (3)
C(5)	1680 (4)	9697 (4)	2719 (11)	70 (2)
C(6)	2202 (3)	9009 (4)	3377 (11)	69 (2)
C(7)	1967 (4)	8765 (4)	5501 (11)	75 (3)
C(8)	1327 (5)	9318 (6)	6054 (12)	82 (3)
O(1)	−578 (3)	8802 (3)	563 (7)	78 (2)
O(2)	1698 (4)	7500	−396 (8)	59 (2)

ᵃ Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**ᵢⱼ tensor.

was performed on a Gow-Mac HPLC with a SiO₂ column and a 7:3 petroleum ether:THF solvent mixture. All new compounds are air-stable as solids.

Toluene, methylene chloride, and hexanes were all purified and distilled under N₂ according to established procedures.[16] *cyclo*-(AsCH₃)₅[17a] and *cyclo*-(AsPh)₆[17b] were prepared by published procedures. [CpRu(CO)₂]₂[13,18] and 1[11b] were prepared by published procedures.

Preparation of {[CpRu(CO)]₂(μ-CO)(μ-AsCH₃)} (2). A dilute solution (10%) of *cyclo*-(AsCH₃)₅ (0.347 g, 0.772 mmol) in dry toluene was added via syringe to a stirring solution of 1 (0.237 g, 0.387 mmol) in 40 mL of toluene. After addition, the reaction was heated to reflux and monitored by IR spectroscopy until no further change in the carbonyl stretching pattern and intensity was seen (1.5 h). During this time, the solution turned cherry

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Table III. Atomic Coordinates (×10⁴) and Isotropic
Thermal Parameters (Å² × 10³) for
[(CpRu(CO))₂(μ-CO)(μ-AsPh)] (3)

	x	*y*	*z*	*U*ᵃ
Ru(1)	3066.8 (5)	3521.9 (1)	4603.5 (5)	32.2 (1)
Ru(2)	3284.4 (4)	4353.0 (1)	2697.9 (5)	31.4 (1)
As	3286.9 (6)	3536.3 (2)	1545.9 (6)	33.2 (2)
O(1)	6672 (5)	3377 (2)	5362 (6)	68 (2)
O(2)	6945 (4)	4399 (2)	3085 (6)	63 (2)
O(3)	3670 (6)	4443 (2)	6481 (5)	63 (2)
C(1)	5299 (7)	3430 (2)	5069 (7)	42 (2)
C(2)	5552 (6)	4378 (2)	2914 (7)	40 (2)
C(3)	3503 (6)	4221 (2)	5260 (6)	38 (1)
C(11)	1036 (7)	2976 (2)	4156 (8)	59 (2)
C(12)	2100 (9)	2843 (3)	5512 (9)	74 (3)
C(13)	2061 (11)	3192 (4)	6790 (8)	118 (4)
C(14)	914 (12)	3538 (3)	6090 (12)	118 (4)
C(15)	331 (8)	3391 (4)	4502 (11)	82 (3)
C(16)	2207 (13)	5087 (3)	2763 (14)	96 (4)
C(17)	2758 (10)	5005 (3)	1181 (15)	105 (4)
C(18)	1869 (11)	4657 (3)	359 (9)	95 (3)
C(19)	753 (8)	4503 (3)	1411 (13)	84 (3)
C(20)	956 (10)	4768 (4)	2778 (10)	96 (4)
C(21)	6231 (7)	3654 (2)	−127 (7)	50 (2)
C(22)	7689 (7)	3521 (2)	−680 (7)	56 (2)
C(23)	8413 (7)	3085 (2)	−175 (7)	56 (2)
C(24)	7675 (7)	2792 (2)	920 (8)	52 (2)
C(25)	6220 (6)	2933 (2)	1489 (7)	47 (2)
C(26)	5489 (6)	3364 (2)	1010 (6)	37 (1)

ᵃ Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U**ᵢⱼ tensor.

Table IV. Selected Bond Distances and Angles for
[(CpRu(CO))₂(μ-CO)(μ-AsCH₃)] (2)

Bond Distances, Å			
Ru–Ru(a)	2.788 (1)	Ru–C(1)	1.851 (5)
Ru–As	2.465 (1)	Ru–C(2)	2.024 (5)
Ru–CNTᵃ	1.917 (6)	C(1)–O(1)	1.138 (7)
As–C(3)	2.001 (7)	C(2)–O(2)	1.183 (8)

Bond Angles, deg			
As–Ru–Ru(a)	55.6 (1)	C(1)–Ru–C(2)	89.8 (2)
Ru–As–Ru(a)	68.9 (1)	C(1)–Ru–As	90.0 (2)
CNT–Ru–As	119.9 (2)	C(1)–Ru–Ru(a)	98.6 (2)
CNT–Ru–Ru(a)	132.2 (2)	C(2)–Ru–As	100.9 (1)
CNT–Ru–C(1)	129.0 (3)	C(2)–Ru–Ru(a)	46.5 (1)
CNT–Ru–C(2)	119.6 (3)	Ru–As–C(3)	111.2 (2)
Ru–C(3)–Ru(a)	87.0 (3)		

ᵃ CNT = Cp ring centroid.

Table V. Selected Bond Distances and Angles for
[(CpRuCO)₂(μ-CO)(μ-AsC₆H₅)] (3)

Bond Distances, Å			
Ru(1)–Ru(2)	2.786 (1)	Ru(2)–C(2)	1.858 (5)
Ru(1)–As	2.451 (1)	Ru(2)–C(3)	2.051 (5)
Ru(2)–As	2.457 (1)	As–C(26)	1.970 (5)
Ru(1)–CNT(1)ᵃ	1.909 (6)	C(1)–O(1)	1.138 (7)
Ru(2)–CNT(2)	1.914 (6)	C(2)–O(2)	1.142 (6)
Ru(1)–C(1)	1.851 (5)	C(3)–O(3)	1.144 (6)
Ru(1)–C(3)	2.042 (5)		

Bond Angles, deg			
Ru(1)–As–Ru(2)	69.2 (1)	CNT(2)–Ru(2)–As	119.2 (1)
As–Ru(1)–Ru(2)	55.5 (1)	CNT(2)–Ru(2)–Ru(1)	133.6 (1)
As–Ru(2)–Ru(1)	55.3 (1)	CNT(2)–Ru(2)–C(2)	129.8 (2)
CNT(1)–Ru(1)–As	119.1 (1)	CNT(2)–Ru(2)–C(3)	120.4 (2)
CNT(1)—Ru(1)–Ru(2)	133.5 (1)	As–Ru(2)–C(2)	91.4 (2)
CNT(1)–Ru(1)–C(1)	130.5 (2)	As–Ru(2)–C(3)	101.4 (1)
CNT(1)–Ru(1)–C(3)	120.1 (2)	C(2)–Ru(2)–C(3)	86.8 (2)
As–Ru(1)–C(1)	90.8 (2)	Ru(1)–C(3)–Ru(2)	85.8 (2)
As–Ru(1)–C(3)	101.9 (1)	Ru(1)–As–C(26)	112.6 (1)
C(1)–Ru(1)–C(3)	86.6 (2)	Ru(2)–As–C(26)	110.3 (1)

ᵃ CNT(1) = Cp(11–15) ring centroid; CNT(2) = Cp(16–20) ring centroid.

red. After completion of the reaction, the volume of the toluene solution was reduced to ∼5 mL, and the reaction mixture was chromatographed on alumina. 2 was eluted as a red band with

10% toluene in hexanes after the starting materials had been removed from the column with 100% hexanes. Crystals were grown from CH_2Cl_2/hexanes in approximately 70% yield; mp 202-204 °C (dec); ^{1}H NMR (CDCl$_3$) δ 5.14 (10 H, s), 2.36 (3 H, s); IR (CHCl$_3$ solution) ν_{CO} 1983 (s), 1946 (m), 1801 (s) cm^{-1}. Anal. Calcd for C$_{14}$H$_{13}$AsO$_3$Ru$_2$: C, 33.21; H, 2.59; As, 14.80. Found: C, 32.93; H, 2.69; As, 14.59.

Preparation of {[CpRu(CO)]$_2$(μ-CO)(μ-AsC$_6$H$_5$)} (3). 2 (0.350 g, 0.59 mmol) and *cyclo*-(AsC$_6$H$_5$)$_6$ (0.54 g, 0.59 mmol) were combined in 100 mL of xylenes, and the reaction was heated to 110 °C overnight under nitrogen. The xylenes were removed from the reaction, and then the residue was placed on an alumina column and eluted with dichloromethane. One red-orange product was isolated off the column in good yield (80%) and identified as 4: mp 240-243 °C; IR (CH$_2$Cl$_2$) ν_{CO} = 1990 (s), 1953 (m), 1780 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.50-7.12 (m, 5 H), 5.30 (s, 10 H). Diffraction-grade crystals were grown from CH_2Cl_2/hexanes. Anal. Calcd for C$_{19}$H$_{15}$AsO$_3$Ru$_2$: C, 40.15; H, 2.66; As, 13.18. Found: C, 39.89; H, 2.75; As, 13.01.

Crystallographic Structure Determinations. Crystallographic data are collected in Table I. For both structures, crystals were mounted on glass fibers, unit-cell parameters were obtained from the angular settings of 25 reflections (30° $\leq$ 2θ $\leq$ 35°), and empirical corrections for absorption were applied to the diffraction data. For 2, the centrosymmetric alternative *Pnma* was suggested by *E* statistics and verified by the presence of mirror-plane symmetry. The structures were solved by direct methods. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were incorporated as idealized contributions (d(CH) = 0.96 Å). Tables II and III contain the atomic coordinates for 2 and 3, and Tables IV and V contain selected bond distances and angles. All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI).

Liquid Crystals Based on Ortho-Palladated Azines: Nonplanar Mesogens

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The synthesis and mesogenic properties of the complexes [Pd(C$_n$H$_{2n+1}$OC$_6$H$_3$CH=N—N=CHC$_6$H$_4$OC$_n$H$_{2n+1}$){μ-O$_2$CCH$_3$}]$_2$ [I(n), n = 2, 6-10, 12, and 14] and [Pd(C$_{10}$H$_{21}$OC$_6$H$_3$CH=N—N=CHC$_6$H$_4$OC$_{10}$H$_{21}$){μ-X}]$_2$ [X = Cl (II), Br (III), and SCN (IV)] are described. Not unexpectedly, II, III, and IV, which are planar dimers, show S$_C$ mesophases. More interestingly the open-book-shaped dimers I(n) also exhibit N and/or S$_C$ mesophases if the alkoxylic chains are sufficiently long (n $\geq$ 6). In spite of their unusual molecular shape, the mesophases resemble those produced by typical rodlike molecules.

Introduction

Organometallic and coordination compounds displaying liquid-crystalline behavior are currently of great interest as new mesogenic materials able to extend or improve the properties of the liquid-crystalline materials so far available, most of which are organic molecules. Linear (as in Ag^I) and square-planar (as in Pd^{II}) coordinations are capable of retaining beyond the melting point the ordered arrangements of individual molecules that give rise to mesogenic behavior, and some compounds containing these elements with liquid-crystal properties have been recently described.[1-6]

We have reported[7-9] some ortho-palladated compounds of imines [Pd(*p*-RC$_6$H$_3$C(Y)=N—C$_6$H$_4$R'-*p*){μ-X}]$_2$ (R, R' = alkyl, alkoxy, and polar groups; Y = H and CH$_3$; X = Cl, Br, SCN, and OAc), many of which were mesogenic even when the free imines were not liquid crystals. It became apparent from these studies that a methyl sub-

Table I. Analytical Data, Molecular Weights (Calculated Values in Parentheses), and Yields

compd	N	C	H	MW	yield, %
I(2)	6.10 (6.08)	51.53 (52.13)	4.70 (4.81)	953 (921.6)	58
I(6)	5.04 (4.89)	58.31 (58.69)	5.99 (6.68)	1201 (1146.1)	37
I(7)	4.47 (4.66)	59.57 (59.95)	7.49 (7.04)	1175 (1202.2)	63
I(8)	4.65 (4.64)	64.10 (63.72)	7.85 (7.68)	1283 (1258.3)	52
I(9)	4.16 (4.26)	61.80 (62.14)	7.99 (7.67)	1391 (1314.4)	55
I(10)	4.16 (4.09)	62.99 (63.10)	7.70 (7.94)	1397 (1370.5)	50
I(12)	3.80 (3.78)	64.44 (64.81)	8.18 (8.43)	1539 (1482.7)	55
I(14)	3.36 (3.27)	62.53 (62.36)	8.21 (8.29)	1560 (1594.9)	43
II	4.34 (4.23)	61.75 (61.72)	7.37 (7.77)	1278 (1323.3)	85
III	4.07 (3.97)	58.14 (57.84)	7.06 (7.28)	1354 (1412.2)	87
IV	6.04 (6.14)	61.85 (61.44)	7.15 (7.51)	1404 (1368.5)	82

stituent in the azomethyne carbon or a bent bridge, such as acetate, diminished mesogenic behavior to such an ex-

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