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Metalation of Alkynes. 5. Reaction of Diphenylethyne with Mercuric Salts in Alcohols. Synthesis, Stereochemistry, and Structure of (β-Alkoxyvinyl)mercury Adducts[1]

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Diphenylethyne (1) has been reacted with mercury(II) acetate and mercury(II) trifluoroacetate in solutions of methanol, ethanol, 2-propanol, and 2-methyl-2-propanol. The reactions with mercury(II) acetate yield the corresponding (β-alkoxyvinyl)mercury adducts, as a mixture of *Z* and *E* isomers, only in methanol and ethanol. Mercury(II) trifluoroacetate reacts in ethanol and 2-propanol with high stereoselectivity, yielding the *Z* isomers of PhC(HgCl)=C(OEt)Ph (**4a**) and PhC(HgCl)=C(OCHMe$_2$)Ph (**5a**), which have been completely characterized by X-ray structure determinations. Mercurated products were not isolated from the reactions in 2-methyl-2-propanol. Crystal data for **4a**: $C_{16}H_{15}ClHgO$, M_r 459.3, monoclinic, space group $P2_1/c$, $a = 8.641$ (2) Å, $b = 19.107$ (3) Å, $c = 9.718$ (3) Å, $\beta = 99.41$ (4)°, $V = 1582.9$ Å^3, $Z = 4$, $D_{calcd} = 1.93$ g cm^{-3}. Crystal data for **5a**: $C_{17}H_{17}ClHgO$, M_r 473.4, monoclinic, space group $P2_1/c$, $a = 8.379$ (2) Å, $b = 22.514$ (2) Å, $c = 9.152$ (3) Å, $\beta = 101.74$ (3)°, $V = 1690.4$ Å^3, $Z = 4$, $D_{calcd} = 1.86$ g cm^{-3}. Alkyl branching of the alcohol solvent reduces the reactivity but enhances the stability of the (β-alkoxyvinyl)mercury adducts.

Introduction

The reaction of an olefin or acetylene with an electrophilic mercuric salt yields adducts in which the mercury moiety and the solvent have added across the carbon–carbon unsaturation. This reaction, called solvomercuration, has become an extremely valuable tool for the functionalization of olefins and acetylenes when coupled with a convenient method for replacing the mercury moiety by hydrogen or other substituents.[2]

The solvomercuration reaction of alkynes in alcohols represents a convenient entry to vinyl ethers, acetals or ketals, dioxanes, or furans depending on the substrate, the solvent, and the general conditions.[3] So far, it has been impossible to stop the reaction at the vinylmercurial stage, except for one case in which the substrate contained the alcohol functionality at the appropriate distance to yield a stable cyclic adduct.[3,4] Alkenylmercurials, which are easily prepared in the form of vinylmercurial acetates,[5] are of synthetic interest, since they can be stereoselectively transformed into butadienes[6] as well as carbonylated to yield symmetrical vinyl ketones[7] or unsaturated esters.[8] We felt that the preparation of vinylmercurial ethers and some understanding of the factors which favor their formation may have an intrinsic interest, as well as a potential application for the functionalization of alkynes.

In the case of olefins, it has been found that the solvomercuration–demercuration procedure carried out in alcohol solvents represents a method of wide generality for the synthesis of ethers.[9]

We recently reported on the reactions and kinetics of several internal alkynes with mercury(II) acetate in methanol and isolated stable (methoxyvinyl)mercurials from a series of arylalkylalkynes.[1] During that study, we realized that the formation and stability of such derivatives were somehow favored by the phenyl substituent on the triple bond and decided that diphenylethyne in particular was a suitable substrate to verify the scope and generality of the reaction in different alcohol solvents.

Results

Reactions of Diphenylethyne (1) with Mercury(II) Acetate. The reaction of diphenylethyne (1) with mercury(II) acetate (Hg(OAc)$_2$) in MeOH was recently described.[1] A mixture of the two geometric isomers of PhC(HgOAc)=C(OMe)Ph (**1a**) in a 3:1 (*E*:*Z*) ratio was obtained in quantitative yield after 24 h at room temperature. The reaction carried out for a shorter time with an excess of mercuric salt indicated that the products were obtained under kinetic control, no equilibration taking place during the time necessary to complete the reaction. Under these conditions, products from demercuration processes were not observed.

In this work, diphenylethyne was reacted with equimolar amounts of mercury(II) acetate in ethanol, 2-propanol, and 2-methyl-2-propanol, at room temperature under nitrogen. The reaction in ethanol, after 72 h, yielded a 1:1 mixture of (*E*)- and (*Z*)-1-(acetoxymercurio)-2-ethoxy-1,2-diphenylethene (**2a**) in 27% yield, estimated by NMR

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Table I. Product Analyses for the Reaction between Diphenylethyne and HgX_2 (X = $MeCO_2$, CF_3CO_2) in Alcohols at Room Temperature[a]

X	ROH	time, h	yield[b] of PhC(OR)=C(HgY)Ph, %	alkene geom	yield[c] of demercurated products, %
$MeCO_2$[d]	MeOH	24	>95[e]	*Z* + *E*, 1:3	
$MeCO_2$	EtOH	72	27[e,f]	*Z* + *E*, 1:1	
$MeCO_2$	*i*-PrOH	100			
$MeCO_2$[g]	AcOH	24	85[h]	*E*	
CF_3CO_2	MeOH	1	3[h]	*Z* + *E*,[i] 2:1	80
CF_3CO_2	EtOH	0.3–5	10–15[h]	*Z*	30–60
CF_3CO_2	*i*-PrOH	24	50[h]	*Z*	25
CF_3CO_2	*t*-BuOH	45			20

[a] Unreacted diphenylethyne is the complement to 100% yield. [b] Isolated products. [c] Determined after workup of the filtrate. [d] Reference 1. [e] Y = $MeCO_2$. [f] Determined by integration of the ^1H NMR spectrum for the crude reaction product. [g] Reference 5e. [h] Y = Cl. [i] Individual isomers were not identified as *E* or *Z*.

spectral analysis of the product mixture, and unreacted diphenylethyne (eq 1). Several attempts to separate the

$$\underset{1}{\mathrm{PhC{\equiv}CPh}} + \mathrm{Hg(OAc)_2} \xrightarrow[72\ \mathrm{h}]{\mathrm{EtOH,\ room\ temp}} \underset{\mathbf{2a}\ (1:1\ E:Z)}{\mathrm{PhC(OEt){=}C(HgOAc)Ph}} \quad (1)$$

mercurated products by crystallization were not successful. From the reactions in 2-propanol and 2-methyl-2-propanol, after several days, unreacted diphenylethyne was recovered quantitatively from the reaction. The results are summarized in Table I.

Because of the poor reactivity exhibited by mercury(II) acetate, we examined the behavior of the more electrophilic mercury(II) trifluoroacetate, $Hg(TFA)_2$.

Reactions of Diphenylethyne (1) with Mercury(II) Trifluoroacetate. Diphenylethyne (1) and mercury(II) trifluoroacetate were allowed to react in solutions of methanol, ethanol, 2-propanol, 2-methyl-2-propanol, and 1-butanol, at room temperature under nitrogen. The corresponding products of alkoxymercuration of the triple bond, when formed, were precipitated from the reaction mixture by addition of aqueous KCl[10] and obtained, after purification, as air-stable pale yellow crystals. Reaction conditions and yields of these (alkoxyvinyl)mercury chloride derivatives are listed in Table I.

The reaction in methanol yielded only trace amounts of mercurated products (**3a**, *E* + *Z*) after 1 h. The reaction mixture, just before addition of KCl, contained some unreacted diphenylethyne, the vinylic isomers from protodemercuration (**3b**), and trace amounts of PhCOCH(OMe)Ph. After separation of the solid vinylmercury derivatives, aqueous workup of the filtrate afforded 1,2-diphenylethanone (**3c**) as the main product (eq 2).

$$\mathrm{PhC{\equiv}CPh} + \mathrm{Hg(TFA)_2} \xrightarrow[1\ \mathrm{h,\ room\ temp}]{\mathrm{MeOH}}$$

$$\begin{array}{c} \mathrm{PhC(OMe){=}C(HgCl)Ph} \\ \mathbf{3a}\ (E + Z),\ 3\% \\ \Big\uparrow \text{aqueous KCl} \\ \mathrm{PhC(OMe){=}C(HgOCOCF_3)Ph} \\ + \\ \mathrm{PhC(OMe){=}CHPh} \\ \mathbf{3b}\ (1:1\ E:Z) \\ \Big\downarrow \mathrm{CH_2Cl_2/H_2O} \\ \mathrm{PhC(O)CH_2Ph} \\ \mathbf{3c} \end{array} \quad (2)$$

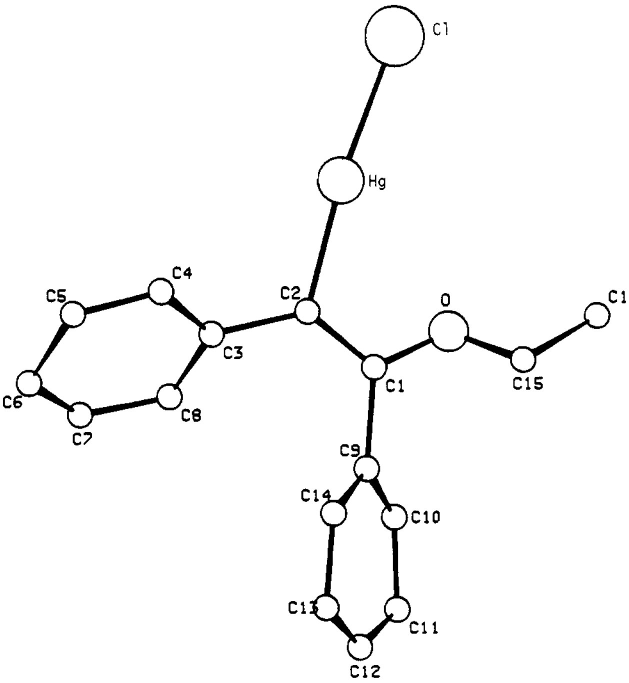

Figure 1. Molecular structure of (*Z*)-PhC(HgCl)=C(OEt)Ph (**4a**).

The reaction in ethanol afforded one isomer of 1-(chloromercurio)-2-ethoxy-1,2-diphenylethene (**4a**) in about 10% yield, after 35 min. Analysis of the reaction mixture after separation of the solid mercurated product and extraction by chloroform/water revealed the presence of unreacted diphenylethyne, of (*E*)- and (*Z*)-1-ethoxy-1,2-diphenylethene (**4b**), and of 1,2-diphenylethanone (**3c**). Several attempts were carried our in order to improve the yield of the mercurated compound by varying the reaction conditions. Extending the reaction time to 5 h and using 2 equiv of mercury(II) trifluoroacetate only resulted in greater formation of the ketone (**3c**) and the absence of the vinyl ethers in the crude reaction mixture. Reducing the reaction time to 15 min and using 3 equiv of the mercurating agent gave 15% of the mercurated vinyl ether but did not prevent the formation of **3b**. In both cases, diphenylethyne was still present in large amounts.

Therefore, the general reaction scheme is similar to that observed in methanol (eq 2). However, both the yield and stability of the isolated vinylmercury derivative are improved on running the reaction in ethanol. Moreover, in this case only the *Z* isomer of 1-(chloromercurio)-2-ethoxy-1,2-diphenylethene (**4a**) was isolated. The crude product was first purified by slow precipitation from warm cyclohexane. ^1H and ^{13}C NMR spectral analysis of the crude and the purified samples gave no evidence for the

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(10) We have recently reported that addition of aqueous KCl to the reaction of diphenylethyne and $Hg(OAc)_2$ in methanol induces a geminal double mercuration of the triple bond: Bassetti, M.; Bocelli, G. *J. Chem. Soc., Chem. Commun.* **1990**, 257. On the other hand, we have found no evidence of a similar process in the use of $Hg(TFA)_2$.

Table II. Bond Distances (Å), Bond Angles (deg), and Selected Torsion Angles (deg) of (*Z*)-PhC(HgCl)=C(OEt)Ph (4a) and (*Z*)-Ph(HgCl)=C(OCHMe$_2$)Ph (5a)

	5a	4a		5a	4a
Hg–Cl	2.320 (3)	2.32 (1)	C6–C7	1.343 (16)	1.34 (3)
Hg–C2	2.055 (10)	2.03 (2)	C7–C8	1.389 (15)	1.41 (3)
O–C1	1.402 (11)	1.34 (2)	C9–C10	1.395 (15)	1.38 (3)
O–C15	1.457 (12)	1.34 (2)	C9–C14	1.383 (13)	1.26 (3)
C1–C2	1.327 (12)	1.33 (2)	C10–C11	1.412 (15)	1.39 (3)
C1–C9	1.500 (14)	1.53 (2)	C11–C12	1.388 (15)	1.29 (4)
C2–C3	1.491 (13)	1.50 (2)	C12–C13	1.398 (17)	1.38 (4)
C3–C4	1.392 (15)	1.42 (2)	C13–C14	1.424 (16)	1.42 (3)
C3–C8	1.382 (13)	1.42 (2)	C15–C16	1.508 (17)	1.51 (3)
C4–C5	1.417 (17)	1.41 (3)	C15–C17	1.483 (16)	
C5–C6	1.393 (19)	1.53 (3)			
Cl–Hg–C2	176.3 (2)	173.6 (4)	C6–C7–C8	119.5 (10)	126.3 (17)
C1–O–C15	117.5 (6)	116.2 (12)	C3–C8–C7	122.1 (8)	119.6 (15)
O–C1–C9	114.9 (7)	117.8 (13)	C1–C9–C14	120.0 (8)	124.7 (17)
O–C1–C2	117.3 (8)	116.7 (13)	C1–C9–C10	120.2 (8)	119.8 (16)
C2–C1–C9	127.8 (8)	124.5 (14)	C10–C9–C14	119.8 (9)	115.5 (18)
Hg–C2–C1	115.1 (6)	114.2 (11)	C9–C10–C11	121.8 (9)	124.7 (20)
C1–C2–C3	125.2 (8)	127.7 (13)	C10–C11–C12	117.3 (10)	113.2 (20)
Hg–C2–C3	119.6 (6)	117.8 (10)	C11–C12–C13	122.4 (10)	128.0 (21)
C2–C3–C8	123.7 (8)	123.0 (15)	C12–C13–C14	118.7 (10)	111.7 (23)
C2–C3–C4	119.1 (9)	118.6 (14)	C9–C14–C13	119.9 (9)	126.2 (23)
C4–C3–C8	117.1 (9)	118.5 (17)	O–C15–C17	109.5 (9)	
C3–C4–C5	121.9 (11)	120.9 (16)	O–C15–C16	106.5 (9)	106.2 (17)
C4–C5–C6	117.0 (11)	120.1 (17)	C16–C15–C17	112.4 (10)	
C5–C6–C7	122.3 (11)	114.4 (18)			
C1–O–C15–C16	−158.5 (9)	175.9 (20)	C9–C1–C2–Hg	−172.2 (8)	178.7 (12)
C1–O–C15–C17	79.7 (11)		C2–C1–C9–C10	43.1 (15)	124.3 (20)
C15–O–C1–C9	56.8 (10)	−54.7 (18)	C2–C1–C9–C14	−135.6 (11)	−52.9 (26)
C15–O–C1–C2	−125.6 (9)	136.2 (14)	C9–C1–C2–C3	12.4 (16)	−8.1 (25)
O–C1–C2–Hg	10.5 (11)	−13.1 (18)	C1–C2–C3–C4	−140.3 (11)	137.3 (18)
O–C1–C9–C10	−139.6 (9)	−43.8 (23)	Hg–C2–C3–C4	44.6 (12)	−49.8 (19)
O–C1–C9–C14	41.8 (12)	129.0 (20)	C1–C2–C3–C8	40.6 (15)	−41.9 (24)
O–C1–C2–C3	−164.8 (8)	160.1 (14)	Hg–C2–C3–C8	−134.5 (9)	131.1 (14)

presence of a second stereoisomer, at least in a quantity larger than 5%.

Yellow needle-shaped crystals were obtained by slow evaporation of a dichloromethane/ethanol solution of the purified sample. The X-ray structure of 4a is illustrated in Figure 1.

The presence of both the demercurated vinyl ethers (**4b**) in the reaction mixture is probably due to isomerization of the initially formed cis isomer into the trans isomer.

The reaction in 2-propanol afforded (*Z*)-1-(chloromercurio)-2-isopropoxy-1,2-diphenylethene (**5a**) in 50% yield, after 24 h. The crude product was crystallized twice from warm cyclohexane, to give yellow crystals. The X-ray structure is shown in Figure 2. This mercurated vinyl ether is slightly more stable in the reaction medium than its ethoxy and methoxy analogues. As in the case of ethanol, only the *Z* isomer was formed in this solvent.

When the reaction was carried out in 2-methyl-2-propanol at room temperature for 45 h, unreacted diphenylethyne and 1,2-diphenylethanone (**3c**) in the ratio 4:1 were recovered quantitatively after aqueous workup, no mercurated species being present. Similar results were obtained from the reaction in 1-butanol at room temperature for 25 h, both diphenylethyne and **3c** being recovered in similar quantities.

Molecular Geometries of 4a and 5a. The molecular structures of PhC(HgCl)=C(OEt)Ph (**4a**) and PhC(HgCl)=C(OCHMe$_2$)Ph (**5a**) are illustrated in Figures 1 and 2, respectively. Bond distances, bond angles, and selected torsion angles of both molecules are reported in Table II. Final atomic coordinates are listed in Tables III–V. Summaries of the crystallographic data are given in Table VI. Only the geometry of compound **5a** has been determined with accuracy. Unfortunately, the crystals of **4a** decomposed during the X-ray analysis, resulting in experimental data of low quality.

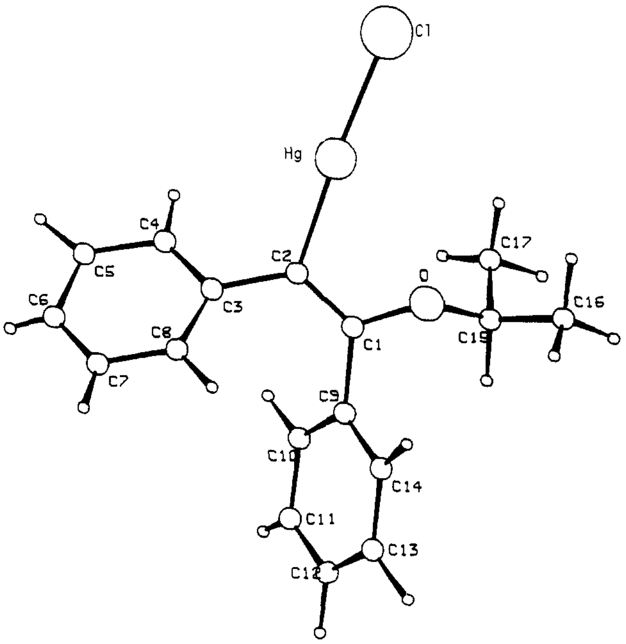

Figure 2. Molecular structure of (*Z*)-PhC(HgCl)=C(OCHMe$_2$)Ph (**5a**).

The X-ray analyses show both the compounds to exist in a cis configuration around the C=C double bond.

The individual aromatic rings in the two molecules are all planar within the error and form a dihedral angle to each other of 124.2 (3)° in **5a** and 122.7 (6)° in **4a**. Probably due to the repulsive phenyl–phenyl interactions, there is some angular strain about the double bond as evidenced by C1–C2–C3 and C2–C1–C9 angles, whose

Table III. Atomic Fractional Coordinates (×10^4) and U_{eq} Values (×10^4 Å^2) for Compound 5a

	x/a	y/b	z/c	U_{eq}
Hg	38653 (5)	41289 (2)	46859 (4)	465 (1)
Cl	5673 (4)	4593 (1)	3443 (3)	687 (11)
O	667 (7)	3680 (3)	3234 (6)	478 (20)
C1	731 (11)	3621 (4)	4770 (10)	393 (30)
C2	2142 (11)	3738 (4)	5680 (10)	420 (31)
C3	2576 (11)	3569 (4)	7287 (11)	463 (35)
C4	3450 (15)	3968 (6)	8308 (13)	628 (45)
C5	3890 (15)	3836 (7)	9852 (13)	702 (45)
C6	3404 (15)	3287 (5)	10312 (14)	626 (46)
C7	2579 (13)	2891 (5)	9347 (12)	576 (43)
C8	2178 (12)	3029 (4)	7837 (11)	512 (34)
C9	−816 (11)	3406 (4)	5178 (11)	455 (33)
C10	−1349 (11)	3652 (5)	6393 (11)	485 (36)
C11	−2789 (13)	3457 (5)	6820 (12)	548 (39)
C12	−3660 (12)	3005 (5)	5985 (13)	547 (39)
C13	−3157 (13)	2745 (5)	4767 (13)	615 (42)
C14	−1700 (13)	2954 (4)	4367 (12)	579 (39)
C15	−592 (12)	4064 (5)	2393 (12)	573 (39)
C16	−831 (19)	3873 (8)	784 (13)	985 (65)
C17	−71 (20)	4693 (5)	2612 (18)	1008 (67)

Table IV. Atomic Fractional Coordinates (×10^4) and U_{eq} Values (×10^4 Å^2) for Compound 4a

	x/a	y/b	z/c	U_{eq}
Hg	6589 (1)	8620 (1)	78 (1)	493 (3)
Cl	4840 (6)	5480 (3)	1546 (6)	675 (17)
O	9707 (13)	13110 (7)	1157 (13)	570 (39)
C1	9680 (16)	12700 (8)	−227 (16)	412 (47)
C2	8290 (15)	11600 (8)	−1011 (16)	367 (43)
C3	7822 (17)	13010 (7)	−2542 (18)	462 (51)
C4	6903 (24)	7930 (9)	−3378 (28)	685 (78)
C5	6507 (22)	8810 (10)	−4828 (22)	667 (76)
C6	7027 (25)	15400 (10)	−5527 (25)	690 (73)
C7	7798 (22)	20060 (9)	−4643 (22)	606 (67)
C8	8272 (22)	19150 (8)	−3197 (22)	565 (54)
C9	11159 (16)	14830 (9)	−792 (18)	491 (53)
C10	11962 (24)	20820 (11)	−296 (30)	807 (95)
C11	13378 (20)	22950 (13)	−650 (33)	745 (86)
C12	13787 (23)	19360 (14)	−1649 (28)	791 (91)
C13	13073 (23)	13460 (15)	−2286 (25)	824 (93)
C14	11700 (24)	11650 (13)	−1738 (30)	802 (94)
C15	10871 (14)	9660 (7)	1957 (12)	294 (37)
C16	10723 (42)	11340 (32)	3452 (22)	2057 (257)

Table V. Atomic Fractional Coordinates (×10^3) for H Atoms and U_{iso} Values (×10^3 Å^2) for 5a

	x/a	y/b	z/c	U_{iso}
H4	401 (19)	427 (60)	816 (17)	175 (61)
H5	470 (10)	402 (33)	1071 (29)	42 (23)
H6	352 (12)	324 (44)	1120 (11)	33 (33)
H7	230 (13)	242 (15)	947 (12)	79 (35)
H8	152 (12)	270 (14)	707 (11)	104 (41)
H10	−64 (14)	400 (49)	709 (12)	116 (36)
H11	−320 (12)	370 (47)	761 (11)	56 (34)
H12	−482 (12)	289 (42)	635 (11)	69 (30)
H13	−407 (13)	239 (15)	403 (13)	85 (76)
H14	−113 (13)	275 (14)	356 (12)	135 (54)
H161	27 (19)	399 (18)	41 (13)	68 (35)
H162	−186 (19)	408 (18)	6 (13)	123 (37)
H163	−98 (19)	340 (18)	75 (13)	109 (40)
H171	104 (20)	473 (15)	219 (18)	46 (42)
H172	8 (20)	490 (15)	369 (18)	154 (48)
H173	−105 (20)	491 (15)	185 (18)	135 (39)
H15	−172 (11)	392 (39)	264 (93)	51 (26)

Table VI. Summary of Crystallographic Data

	5a	4a
formula	$C_{17}H_{17}ClHgO$	$C_{16}H_{15}ClHgO$
mol wt	473.4	459.3
space group	$P2_1/c$	$P2_1/c$
cell const		
a, Å	8.379 (2)	8.641 (2)
b, Å	22.514 (2)	19.107 (3)
c, Å	9.152 (3)	9.718 (3)
β, deg	101.74 (3)	99.41 (4)
cell vol, Å^3	1690.4	1582.9
Z	4	4
D(calcd), g cm^{-3}	1.86	1.93
radiatn, Å	Mo Kα, 0.71069	Mo Kα 0.71069
μ, cm^{-1}	92.57	98.82
F(000)	896	863
decay of std rfln, %	0	19–23
no. of rflns collected	4328	4763
no. of rflns obsd	2085 ($>2\sigma(I)$)	2211 ($>3\sigma(I)$)
R_{int}	0.056	0.14
R	0.034	0.086
R_w[a]	0.036	

[a] $w = 0.27140(\sigma^2 F + 0.00399F^2)$.

values are 125.2 (9) and 127.8 (9)° in **5a** and 127.7 (13) and 124.5 (14)° in **4a**. The dihedral angles between the planes defined by O,C1,C9 and Hg,C2,C3 are 167.2 (7)° in **5a** and 161.4 (12)° in **4a**, indicating a slight deviation from planarity of the π system.

The Hg–C and Hg–Cl distances are 2.03 (2) and 2.32 (1) Å in **4a** and 2.055 (10) and 2.320 (3) Å in **5a**, respectively. The small deviations from linearity of the C2–Hg–Cl bonds are probably a result of packing effects. The mercury atom is weakly bonded to the oxygen of the same molecule, the distances being 2.92 (6) Å in **5a** and 2.86 (11) Å in **4a**. These interactions can be compared with the sum of van der Waals radii of mercury and oxygen (1.51 + 1.40 = 2.91 Å).[11] Moreover, in both molecules, the Hg atom has an intermolecular contact with a chlorine atom (compound **5a**, Hg···Cl^{i} = 3.33 (2) Å, i = $1 - x$, $1 - y$, $1 - z$; compound **4a**, Hg···Cl^{ii} = 3.26 (6) Å, ii = $1 - x$, $1 - y$, $1 - z$).

Crystal structures of vinylmercurials have been reported.[5c,e,12] The C═C bond distances in **4a** (1.33 Å) and **5a** (1.327 Å) are slightly longer than the value of 1.28 Å observed for bis(*trans*-β-styryl)mercury (Hg(CH═CHPh)$_2$)[12b] and of 1.31 Å observed for (*E*)-3-acetoxy-4-(acetoxymercurio)-3-hexene.[5c] This could be indicative of π-electron delocalization through the C–O bond in **4a** and **5a**. In fact, the C1–O bond lengths are 1.402 (11) Å in **5a** and 1.34 (2) Å in **4a**, compared to 1.43 Å found for the C–OAc distance of the compound in ref 5c. The Hg–C distances are very similar in all these vinylmercury derivatives. Other geometrical parameters of **4a** and **5a** are all as expected.

Effect of Pyridine as a Chemical Shift Reagent. Pyridine has been found to produce chemical shift variations of acetoxy or alkoxy groups α to a C–HgX moiety when added to solutions of vinylmercurial acetates[5c] or alkylmercurial ethers.[13] This effect has proved to be very useful for assigning the structures of the isomers obtained from oxymercuration of alkynes or alkenes. It was established that alkoxy groups from a syn addition to the unsaturated bond experience resonance shifts larger than those observed in the compounds from an anti addition.

The addition of excess pyridine to **4a** and to **5a** in $CDCl_3$ induced upfield shifts of the OCH_2 and OCH resonances, respectively, in the range of 1–4 Hz, depending on the amount of pyridine (see Experimental Section). In the mixture of (*E*)- and (*Z*)-PhC(HgOAc)═C(OMe)Ph (**1a**), added pyridine produced a downshift shift up to 1.49 Hz

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of the methoxy resonance at δ 3.51 and an upfield shift up to 4.22 Hz of that at δ 3.43. On the basis of the larger variation for the latter peak and the shift direction similar to that observed in **4a** and **5a**, this peak is assigned to the *Z* isomer of **1a**. The isomeric ratio 3:1 (*E*:*Z*) is therefore established from these experiments.

Discussion

Mercurated vinyl ethers have been reported to be unstable compounds[3] and, as such, difficult to isolate and characterize. In this paper we confirm our preliminary results on the formation of (methoxyvinyl)mercury derivatives from the reaction of diphenylethyne and a series of substituted internal alkynes with mercury(II) acetate in methanol.[1] In fact, we have now isolated and examined by X-ray diffraction (*Z*)-1-(chloromercurio)-2-ethoxy-1,2-diphenylethene (**4a**) and (*Z*)-1-(chloromercurio)-2-isopropoxy-1,2-diphenylethene (**5a**), obtained from diphenylethyne and mercury(II) trifluoroacetate in ethanol and 2-propanol, respectively.

The results obtained in the reactions of diphenylethyne with mercury(II) acetate and mercury(II) trifluoroacetate in different alcohols can be discussed in terms of reactivity and stereochemistry.

Mercury(II) acetate afforded a mixture of (*E*)- and (*Z*)-1-(acetoxymercurio)-2-alkoxy-1,2-diphenylethene from the reaction in methanol, in quantitative yield, and in ethanol, in low yield. This reagent proved unreactive toward longer chain alcohols. In terms of reaction intermediates, the observed stereochemistry is in agreement with either competitive syn and anti attack of a solvent molecule on a bridged cationic species[14] or the formation of open carbonium ions which can produce the two stereoisomers.

In the oxymercuration of alkenes, the structure of the intermediate, whether an open carbocation or a bridged mercury cation, has been a matter of extensive mechanistic investigation and of controversy as well.[15,16]

In the case of alkynes, fewer studies have been carried out. Detailed investigations have been reported concerning the stereochemistry of acetoxymercuration. The reaction with alkylphenylacetylenes proceeds completely in a trans fashion and a bridged mercury cation has been proposed as the intermediate.[5a] Simple dialkylacetylenes also react by an anti addition,[5c,d] as well as diphenylethyne, according to a recent X-ray structure determination.[5e] Previous work reported the formation of only the syn adduct from diphenylethyne[5a,c] and of both (*Z*)- and (*E*)-vinylmercurials in the oxymercuration of diphenylethyne[17] and 2-butyne.[18]

Thus, the high stereoselectivity exhibited by mercury(II) acetate in acetic acid is not retained in methanol and ethanol, where both adducts were isolated from the reaction of diphenylethyne.

These findings indicate that (1) in favorable cases, bridged cationic species are likely intermediates for the reactions of acetylenes as well as olefins and (2) the resulting stereochemistry is also dependent on the solvent.

With mercury(II) trifluoroacetate, low stereoselectivity was observed in methanol. In contrast, only one mercurated stereoisomer was isolated from the reactions in ethanol and 2-propanol. In both cases the *Z* adducts of PhC(OR)=C(HgCl)Ph (R = Et (**4a**), Me_2CH (**5a**)) were obtained in moderate yields. This indicates that diphenylethyne reacts predominantly in a syn fashion, in alcohol solvents. It is possible that (1) such a symmetric alkyne favors the formation of a symmetric bridged species and (2) the steric hindrance of the two phenyl groups prevents solvent attack from the anti position.

Whereas only mercurated adducts or mercurated adducts and substrate were isolated from the reactions with mercury(II) acetate, use of the trifluoroacetate salt resulted in extensive formation of demercurated products in all solvents. In the stronger acidic medium produced by $Hg(TFA)_2$, the mercurated vinyl adducts afford, by protodemercuration, the corresponding vinyl ethers. It is worth noting, however, that the higher electrophilic character of this reagent makes possible the formation of the mercury adduct in 2-propanol, a solvent in which mercury(II) acetate is unreactive.

Two effects were observed by varying the alkyl branching of the alcohol solvent. (1) Higher yields of mercurated adducts were obtained on going from methanol to ethanol to 2-propanol with use of $Hg(TFA)_2$. The size of the alkoxy group gives stability to the product in the acidic medium. (2) The reactivity decreased with higher branching. In fact, reactions with $Hg(TFA)_2$ were longer in 2-propanol (24 h) than in ethanol (1 h) and reactions with $Hg(OAc)_2$ gave lower yields in ethanol (27%) than in methanol (quantitative).

In conclusion, the reactivity decreases from mercury(II) trifluoroacetate to mercury(II) acetate, as expected, and from methanol to ethanol to 2-propanol.

With the limitation that only a comparison between two compounds is possible, there appears to be a correlation between the stability of **4a** and **5a** and their relative C–O bond distances. The shorter C1–O bond in **4a** (1.34 Å) indicates a greater double-bond character than in **5a** (1.402 Å) and higher electron density on the carbon (C2) bonded to mercury, according to classical resonance forms. In line with this, the Hg–C2 carbon of **4a** is found at δ 134.1 and that of **5a** at δ 135.2, which is at 1.1 ppm lower field. This may result in the observed higher reactivity of **4a** toward protodemercuration, which proceeds by a rate-determining attack of a proton on the metal-bonded carbon.[19]

Experimental Section

General Data. ^1H NMR spectra were recorded on a Bruker WP-80 spectrometer with $CDCl_3$ as the solvent, and chemical shifts were reported in parts per million downfield from tetramethylsilane. ^{13}C NMR spectra were obtained on a Varian XL 300-MHz spectrometer in $CDCl_3$ solutions. Gas chromatography/mass spectrometry (GC/MS) analyses were obtained on a HP 5970B system, coupled with a HP 5890 GC instrument, using a 12 m × 0.2 mm silica capillary column coated with methyl silicone gum. IR spectra were measured with a Nicolet FT 510 instrument in the solvent subtraction mode, using 0.1-mm CaF_2 cells. Melting points were taken on a Buchi 510 apparatus and are uncorrected. Microanalyses were obtained from the Microanalysis Service of the CNR "Area di Ricerca", Montelibretti, Roma, Italy.

Diphenylethyne, mercury(II) acetate, and mercury(II) trifluoroacetate were commercially available reagent grade products

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and were used without further purification. Methanol, ethanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol were Carlo Erba RPE-ACS solvents.

Reactions with $Hg(OAc)_2$. In MeOH. The preparation of (*E* + *Z*) PhC(HgOAc)=C(OMe)Ph (**1a**) is described in ref 1. Addition of pyridine to 16 mg of **1a** in 0.5 mL of $CDCl_3$ containing 1% tetramethylsilane induced variations of the two methoxy resonances, as follows: 15, 50, and 150 μL of pyridine produced downfield shifts of 0.28, 0.93, and 1.49 Hz of the peak at δ 3.51 and upfield shifts of 0.33, 1.71, and 4.22 Hz of the peak at δ 3.43, respectively.

In EtOH. Mercury(II) acetate (3.66 g, 0.011 mol) was added to a solution of diphenylethyne (2.0 g, 0.011 mol) in 150 mL of ethanol, the system being kept under nitrogen. The suspension was stirred for 72 h at room temperature; then the solvent was removed under vacuum. The crude reaction product was treated with dichloromethane and the insoluble mercury(II) acetate separated by filtration. Evaporation of the solvent from the clear yellow filtrate left a thick solid, which was extracted several times with hexane to separate insoluble inorganic material. Removing the hexane gave 2.76 g of a yellow oil, which slowly turned into a solid. ^{1}H NMR (δ): 7.8–7.0 (m, Ph); 3.70 (q, *J* = 7.0 Hz) and 3.46 (q, *J* = 6.9 Hz) (2 H, $-OCH_2Me$); 2.08 (s, 3 H, $MeCO_2Hg$); 1.4–1.0 (complex, superimposed quartets, 3 H, $-OCH_2Me$). GC analyses revealed the presence of a large amount of unreacted alkyne, products from demercuration not being detected. The yield of the mercurated products was calculated to be ca. 27% by integration of the ^{1}H NMR spectrum. Attempts to separate by crystallization the mercury-containing species from unreacted diphenylethyne yielded only insoluble inorganic material.

Reactions with $Hg(TFA)_2$. In EtOH: Preparation of (*Z*)-PhC(HgCl)=C(OEt)Ph (4a). Diphenylethyne (2.0 g, 0.011 mol) and mercury(II) trifluoroacetate (4.8 g, 0.011 mol), dissolved in 100 mL of ethanol, were stirred for 30 min at room temperature under nitrogen. Addition of 50 mL of aqueous KCl (15% v/v) resulted in the formation of a white solid, which was collected on a glass filter and air-dried by suction. Treatment of the solid with dichloromethane gave a suspension that, after addition of anhydrous sodium sulfate, was filtered.

Evaporation of dichloromethane yielded 0.50 g of a yellow solid. The crude reaction product was crystallized in warm cyclohexane: mp 133–134 °C; yield 10%. Anal. Calcd for $C_{16}H_{15}OHgCl$: C, 41.84; H, 3.29; Cl, 7.72. Found: C, 41.76; H, 3.27; Cl, 6.88. ^{1}H NMR (δ): 7.4–6.8 (m, 10 H, Ph); 3.69 (q, *J* = 6.99 Hz, 2 H, $-OCH_2Me$); 1.25 (t, *J* = 7.0 Hz, 3 H, *Me*). IR (CCl_4): 1612, 1597 cm^{-1} (C=C). ^{13}C NMR (δ): 157.8 (=COEt); 134.1 (=CHgCl); 139.2, 133.3, 129.9, 129.6, 128.8, 128.3, 126.1 (Ph); 65.3 ($-OCH_2Me$); 15.4 (Me). The assignment of the ethoxy-substituted vinyl carbon was made by comparison with literature data.[20] For the chloromercurio-substituted carbon, a shorter acquisition time and stronger impulse resulted in a large intensity reduction of the attributed peak, the other peaks being virtually unaffected. Crystallization from ethanol/dichloromethane afforded yellow needles suitable for X-ray analysis.

The filtrate was extracted from $CHCl_3$/water to give 2.3 g of an orange liquid, diphenylethyne being the largest component (60% based on GC). Elution with chloroform on silica gel gave diphenylethyne, a mixture of the *E* and *Z* isomers of 1-ethoxy-1,2-diphenylethene (**4b**; *m/e* 224; ^{1}H NMR δ 6.07 and 5.82 (two s, =CH–)), and 1,2-diphenylethanone (**3c**; *m/e* 196; ^{1}H NMR δ 4.29 (s, $-CH_2-$)).

Addition of 20 and 50 μL of pyridine to 8 mg of **4a** in 0.5 mL of $CDCl_3$ produced upfield shifts of 1.6 and 4.3 Hz, respectively, of the central peaks at δ 3.64 and 3.73 in the quartet of the OCH_2 resonance.

In $(Me)_2CHOH$: Preparation of (*Z*)-PhC(HgCl)=C($OCHMe_2$)Ph (5a). Diphenylethyne (1.0 g, 5.6 mmol) and mercury(II) trifluoroacetate (2.4 g, 5.6 mmol) were mixed and dissolved in 100 mL of 2-propanol, under nitrogen, and the mixture was stirred at room temperature for 24 h. A 50-mL amount of 10% aqueous KCl was added and the mixture stirred for 1 h. The white precipitate formed was filtered, washed with some hexane, air-dried by suction, and then suspended in $CHCl_3$. Addition of anhydrous sodium sulfate, filtration, and removal of the solvent gave 0.66 g of a yellow thick solid, corresponding to a pure product on the basis of the ^{1}H NMR spectrum; yield 50%. Two crystallizations in warm cyclohexane yielded yellow thick crystals, mp 172–173 °C. Anal. Calcd for $C_{17}H_{17}OHgCl$: C, 43.14; H, 3.62; Cl, 7.49. Found: C, 42.34; H, 3.50; Cl, 7.28. ^{1}H NMR (δ): 7.3–6.8 (m, 10 H, Ph); 4.02 (heptet, *J* = 6.1 Hz, 1 H, $-OCHMe_2$); 1.23 (d, *J* = 6.1 Hz, 6 H, $-OCHMe_2$). IR (CCl_4): 1609, 1596 cm^{-1} (C=C). ^{13}C NMR (δ): 156.9 (=$COCHMe_2$); 135.2 (=CHgCl); 139.3, 133.8, 129.9, 129.7, 128.8, 128.30, 128.27, 126.1 (Ph); 70.6 ($-OCHMe_2$); 22.2 (Me_2).

Addition of 20 and 50 mL of pyridine to 11 mg of **5a** induced upfield shifts of 0.85 and 2.22 Hz, respectively, of the central peak in the OCH heptet at δ 4.02.

In MeOH. The quantities and the procedure were as described for the reaction in EtOH. The reaction time was 1 h. The white solid formed upon addition of KCl changed rapidly to yellow, and the workup had to be carried out as quickly as possible. Removal of dichloromethane yielded 0.15 g of a gummy yellow solid, yield 3%. ^{1}H NMR (δ): 7.8–7.0 (m, 10 H, Ph); 3.16 and 3.45 (two s, intensity ratio 2.3:1, 3 H, –OMe). The compound decomposed in $CDCl_3$ solution, giving extensive precipitation of a white solid in 15–30 min. Gas chromatographic–mass spectral analysis on the reaction mixture, just before addition of KCl, gave the following: diphenylethyne (1, retention time (rt) 5.5 min, *m/e* 178, 18%), (*E*)- and (*Z*)-1-methoxy-1,2-diphenylethene (**3b**, rt 5.9 and 6.9 min, *m/e* 210, 29 and 43%), and 2-methoxy-1,2-diphenylethanone (rt 7.8 min, *m/e* 225, 7%).

Crystal Structure Determinations of 4a and 5a. Intensities were collected on a Philips PW/1100 single-crystal diffractometer interfaced with a IBM PS2/30 personal computer in the range of 3–26° for compound **5a**, while a CAD_4 diffractometer in the range 3–28° was employed for compound **4a**. Suitable crystals for X-ray diffraction were prisms of about 0.3 × 0.3 × 0.6 and 0.4 × 0.5 × 0.8 mm for **4a** and 0.3 × 0.6 × 0.9 mm for **5a**. Compound **4a** was sealed in a Lindemann capillary under a nitrogen atmosphere. The X-ray beams were circles of 1.5-mm diameter in both diffractometers. For both compounds lattice parameters were refined with use of the angular values of 25 reflections accurately centered on the diffractometers. A check reflection, monitored every 50 counts, did not show any variation for **5a**, while compound **4a** underwent decomposition. Two crystals of **4a** were used for the data collection. The first specimen was changed when it decomposed 19%, while the intensity of the second one decreased about 23% at the end of the data collection time. Both data sets of compound **4a**, corrected for the intensity decay of three standard reflections measured every 50 reflections, were scaled with use of the values of the three standard reflections measured at the beginning of the data collection procedure. The data of both compounds were also corrected for Lorentz and polarization effects. Crystal data and experimental details are in Table VI. The absorption corrections were made by following the method of Walker and Stuart[21] with a program written by Ugozzoli.[22]

Both structures were solved by direct methods with SHELX76[23] and refined through full-matrix least squares with anisotropic thermal parameters. A subsequent difference Fourier map resulted in the location of all the hydrogens for **5a**, while they were not found for **4a**. All hydrogens were refined isotropically. Weights were introduced in the final least-squares cycles for compound **5a**. Unitary weights were used for **4a**, as the weighting scheme $w = 1/[(\sigma^2(F_o) + k(F_o)^2]$, attempted with different *k* values, gave unsatisfactory results. Scattering factors were those of SHELX76. All the calculations were performed on a IBM PS2/80 personal computer with the CRYSRULER package.[24]

Acknowledgment. We wish to thank Professor Barbara Floris for the inspiration of this work, Professor

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Registry No. 1, 501-65-5; (*E*)-**2a**, 127971-26-0; (*Z*)-**2a**, 127971-27-1; (*E*)-**3a**, 127971-30-6; (*Z*)-**3a**, 127971-31-7; (*E*)-**3b**, 19191-03-8; (*Z*)-**3b**, 19202-54-1; **3c**, 451-40-1; **4a**, 127971-28-2; **5a**, 127971-29-3; mercury(II) acetate, 1600-27-7; mercury(II) trifluoroacetate, 13257-51-7.

Supplementary Material Available: Listings of thermal parameters for **4a** and **5a** (1 page); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

EPR Studies of M(CO)$_5^-$ Radicals (M = Cr, Mo, W) Trapped in Single Crystals of PPN$^+$HM(CO)$_5^-$†

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γ-Irradiated single crystals of PPN$^+$HM(CO)$_5^-$ (M = Cr, Mo, W) exhibit persistent anisotropic EPR spectra that are assigned to the free radical ($S = {}^1/_2$) anion metal carbonyls M(CO)$_5^-$. Measurements of the *g* and metal hyperfine interaction anisotropies in crystallographically aligned single-crystal specimens at 77 K are consistent with square-pyramidal geometries for the radicals and unpaired spin densities largely confined to metal d$_{z^2}$ atomic orbitals. A full structure of the W-containing host crystal was established by X-ray diffractometry (space group $P2_1/c$, a = 13.302 (11) Å, b = 20.041 (15) Å, c = 16.074 (7) Å, β = 102.56 (6)°, Z = 4), and unit cell parameters were measured for the isomorphous Cr (a = 13.2413 (22) Å, b = 20.1480 (24) Å, c = 15.9510 (20) Å, β = 102.33 (12)°) and Mo (a = 13.266 (18) Å, b = 20.09 (5) Å, c = 16.07 (8) Å, β = 102.57 (8)°) hosts. In spite of a poor structural refinement (R = 0.13), attributed to high thermal motion and crystal decay, the correlation of tensor principal directions with crystallographic directions was very good. In the case of the Cr compound, a further weak EPR spectrum is ascribed to an antiferromagnetically coupled pair of Cr(CO)$_5^-$ radicals that corresponds to one specific pair of nearest neighbor anions in the crystal structure.

Introduction

The structures of pentacoordinate transition-metal complexes hold a particular fascination for spectroscopists because of the near equality in energy of square-pyramidal and trigonal-bipyramidal geometries and the ease of interconversion between them.[1] In many instances, the pentacoordinate species are reactive intermediates on the pathway between tetracoordinate and hexacoordinate complexes, and their spectroscopic detection calls for special isolation techniques. Our particular interest lies in paramagnetic transition-metal carbonyls, which we endeavor to trap in single-crystal hosts for subsequent examination by electron paramagnetic resonance (EPR) spectroscopy.[2] One of the first investigations that we undertook in this area was the study[3] of the Fe(CO)$_5^+$ radical cation produced by γ-irradiation of the neutral carbonyl trapped in single crystals of Cr(CO)$_6$. Examination of the **g**, ^{13}C hyperfine, and ^{57}Fe hyperfine tensors proved conclusively that the radical in Cr(CO)$_6$ had square-pyramidal geometry with much of the unpaired spin density located in a Fe 3d$_{z^2}$ orbital. This conclusion reinforced inferences drawn from contemporary powder spectroscopic studies that the isoelectronic species Mn(CO)$_5$,[4-10] Re(CO)$_5$[11-13] and M(CO)$_5^-$ (M = Cr, Mo, W)[14] also have C_{4v} geometry. Phosphine-substituted manganese[15] and rhenium[16] carbonyls appear to retain this geometry, whereas phosphine-substituted iron carbonyl cations and acyl-substituted iron carbonyls[17] adopt a trigonal-bipyramidal geometry.

Table I. Summary of X-ray Diffraction Data

compd	PPN$^+$HW(CO)$_5^-$
formula	$C_{41}H_{31}NO_5P_2W$
fw	863.50
a, Å	13.302 (11)
b, Å	20.041 (15)
c, Å	16.074 (7)
α, deg	90.00
β, deg	102.56 (6)
γ, deg	90.00
V, Å^3	4182.5
Z	4
ρ_{calcd}, g cm^{-3}	1.371
space group	$P2_1/c$
cryst dimens, mm	0.40 × 0.40 × 0.07
temp, °C	18
radiation	Mo Kα
μ, cm^{-1}	29.4
data collection	ω–2θ
max 2θ, deg	42.0
scan speed, deg min^{-1}	2
scan width, deg	1
total no. of observns	5340
no. of unique data, $I > 2.5\sigma(I)$	2031
final no. of variables	261
final max shift/error	1.198
max residual density, e Å^{-3}	1.79
R^a	0.132
$R_w{}^b$	0.157

$^a \sum||F_o| - |F_c||/\sum|F_o|$. $^b [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

In order to explore the geometry and electronic structure of the group 6 pentacarbonyl anion radicals, we chose to examine[18] radiation-damaged single crystals of PPh$_4^+$HCr(CO)$_5^-$. To our surprise, the radical Cr(CO)$_5^-$ in that

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