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Facile Alkyne Coupling Reactions in Dirhenium Carbonyl Complexes

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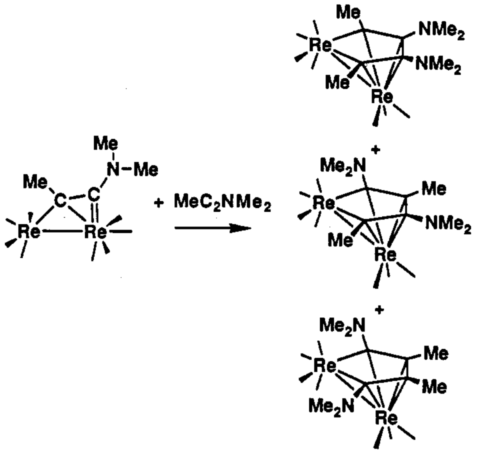
The complex $(OC)_4Re[\mathit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ (**1**) was converted to the reactive acetonitrile complex $(OC)_4Re[\mathit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ (**2**) by reaction with Me_3NO in acetonitrile. Under an atmosphere of CO, complex **2** reacts with $HC{\equiv}CCO_2Me$ in refluxing CH_2Cl_2 to yield the new complexes $(OC)_4Re[\mu\text{-}C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]\text{-}Re(CO)_5$ (**3**; 11%) and $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (**4a,b**; 49%, existing in solution as a mixture of isomers) by the head-to-tail coupling of two and three $HC{\equiv}CCO_2Me$ molecules, respectively. In the absence of CO only compound **4** and a small amount of the new compound $Re(CO)_4[C_6H_2(CO_2Me)(CO_2Me)_2]$ (**5**; 6%) were obtained. Complex **3** was converted into **4** by reaction with additional $HC{\equiv}CCO_2Me$ in the presence of Me_3NO. When heated to 98 °C, **4** was transformed into **5** in 22% yield. Three of the products, **3**, **4a**, and **5** were characterized crystallographically. In complex **3** the two linked $HC{\equiv}CCO_2Me$ groups form a four-carbon chain between the metal-containing groups. One of the carboxylate substituents is also coordinated to form a five-membered metallacyclic ring. In complex **4a** the metal-containing groups are joined by a six-carbon chain formed from the three alkynes, and two of the carboxylate groups are coordinated to form five- and six-membered metallacyclic rings. The six-carbon chain in **4** was transformed into a 2,4,6-tris(methoxycarbonyl)phenyl group that is σ-coordinated to the metal atom and also has one of its carboxylate groups coordinated. Crystal data: for **3**, space group $P\bar{1}$, $a = 13.792(2)$ Å, $b = 14.009(2)$ Å, $c = 6.2734(6)$ Å, $\alpha = 91.47(1)°$, $\beta = 92.95(1)°$, $\gamma = 114.764(8)°$, $Z = 2$, 2120 reflections, $R = 0.023$; for **4a**, space group $P\bar{1}$, $a = 10.7738(8)$ Å, $b = 13.179(2)$ Å, $c = 9.024(1)$ Å, $\alpha = 96.52(1)°$, $\beta = 101.467(8)°$, $\gamma = 84.604(9)°$, $Z = 2$, 2428 reflections, $R = 0.024$; for **5**, space group $P\bar{1}$, $a = 9.947(1)$ Å, $b = 11.840(2)$ Å, $c = 7.977(1)$ Å, $\alpha = 106.99(1)°$, $\beta = 102.98(1)°$, $\gamma = 89.52(1)°$, $Z = 2$, 1968 reflections, $R = 0.022$.

Introduction

The oligomerization and polymerization of alkynes has led to a variety of new compounds and materials.[1,2] Metal complexes have been shown to be very effective in promoting these reactions.[3] Most metal-promoted alkyne coupling reactions occur by the coordination of the alkyne followed by the insertion of the alkyne into a metal–carbon bond.[4] The reactions of diphenylacetylene with $Re_2(CO)_{10}$[5] and $H_3Re_3(CO)_{12}$[6] have yielded dirhenium complexes containing metallacycles formed by the coupling of two or more alkynes. We have recently prepared the complex $Re_2(CO)_8(\mu\text{-}MeCCNMe_2)$, which has a bridging $MeC{\equiv}CNMe_2$ group, and have shown that it reacts with an additional equivalent of $MeC{\equiv}CNMe_2$ to form three isomeric metallacyclic complexes through head-to-head, head-to-tail, and tail-to-tail coupling of the ynamines (eq 1).[7] The reactions of $Re_2(CO)_9(NCMe)$ with alkynes containing carboxylate groups yields the dimetalated-olefin complexes $Re(CO)_4[\mathit{trans}\text{-}\mu\text{-}RC{=}C(CO_2Me)]Re\text{-}(CO)_5$ (A) by the insertion of the alkyne into the metal–metal bond.[8]



(1)

When treated with Me_3NO in MeCN, the complex $Re\text{-}(CO)_4[\mathit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ (**1**) is trans-

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[1] (a) Hoogzand, C.; Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; Vol. 1, pp 343-369. (b) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Wiley: New York, 1975; Vol. 2, pp 213-245.

[2] (a) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1 and 2. (b) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Material Science*; Academic: Orlando, FL, 1984.

[3] (a) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 52, pp 410-413. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

[4] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science, Mill Valley, CA, 1987; Chapter 11, p 608.

[5] Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* 1981, 771.

[6] Pourreau, D. B.; Whittle, R. R.; Geoffroy, G. L. *J. Organomet. Chem.* **1984**, *273*, 333.

[7] Adams, R. D.; Chen, G.; Yin, J. *Organometallics* **1991**, *10*, 1278.

[8] (a) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1992**, *11*, 3505. (b) Adams, R. D.; Chen, L.; Wu, W. *Organometallics*, in press.

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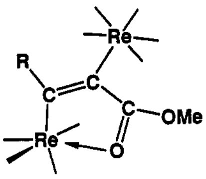

A

formed into the lightly stabilized complex $Re(CO)_4$[*trans*-μ-$HC{=}C(CO_2Me)$]$Re(CO)_4(NCMe)$ (2), which readily reacts with carboxylate-substituted alkynes to form oligomeric chains of the alkynes by head-to-tail coupling. The results of this study are reported here.

Experimental Section

All reactions were carried out under atmosphere of nitrogen. Hexane and heptane were freshly distilled over sodium before use. Acetonitrile and CH_2Cl_2 were dried over CaH_2 before use. $Me_3NO{\cdot}2H_2O$ was dehydrated by sublimation. Traces of water were removed from the commercially purchased CO by passing it through a column of P_2O_5. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were run on a VG Model 70SQ mass spectrometer. $(OC)_4Re$[*trans*-μ-$HC{=}C(CO_2Me)$]$Re(CO)_5$ (1) was prepared by the previously reported procedure.[8]

Preparation of $(OC)_4Re$[*trans*-μ-$HC{=}C(CO_2Me)$]$Re(CO)_4(NCMe)$ (2). A 100-mg amount (0.141 mmol) of $(OC)_4Re$[*trans*-μ-$HC{=}C(CO_2Me)Re(CO)_5$ (1) was dissolved in 25 mL of MeCN. An 11.7-mg amount (0.155 mmol) of Me_3NO was added, and the solution was stirred at 25 °C for 5 min. The solvent was then evaporated under a stream of nitrogen at 25 °C to yield 72.0 mg (71%) of pale yellow crystals of 2. IR (ν_{CO}, in CH_2Cl_2, cm^{-1}) for 2: 2098 (w), 2084 (m), 1996 (s, br), 1936 (s), 1914 (s), 1539 (w, br). ^1H NMR (δ, in C_6D_6) for 2: 10.52 (s, 1H, CH), 3.35 (s, 3H, OCH_3), 0.25 (s, 3H, CCH_3). The mass spectrum of 2 showed the parent ion *m/e* 721 and ions corresponding to the loss of each of the nine carbonyls and one acetonitrile ligand. Compound 2 was unstable on silica gel and is also sensitive to H_2O when in solution.

Preparation of $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$ (3). Under an atmosphere of CO, a 30-mg amount (0.041 mmol) of 2 and a 100-μL (1.25 mmol) amount of $HC{\equiv}CCO_2Me$ were dissolved in 10 mL of CH_2Cl_2. The solution was heated to reflux in the presence of a slow CO purge for 4 h. After it was cooled, the solution was evaporated to dryness. The residue was separated by TLC using a 1/1 CH_2Cl_2/hexane solvent mixture to give 3.5 mg of pale yellow $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$ (3; 11% yield) and 17.0 mg of $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (4, a mixture of the two isomers 4a and 4b; 49% yield). One isomer of compound 4 (hereafter referred to as 4a) was obtained by crystallization of the mixture from the upper part of the yellow band containing 4a and 4b on the plate. Attempts to obtain 4b in pure form by chromatographic separation and fractional crystallization were unsuccessful. IR (ν_{CO}, in hexane, cm^{-1}): for 3, 2135 (w), 2097 (w), 2068 (w), 2025 (w), 2016 (m), 1994 (s), 1985 (s), 1947 (s), 1731 (m, br), 1683 (w, br), 1632 (w, br); for 4a, 2101 (w, sh), 2097 (w), 2002 (s), 1983 (m), 1953 (m), 1731 (w), 1633 (w, br), 1590 (w, br). ^1H NMR (δ, in $CDCl_3$): for 3, 9.62 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, CH), 7.66 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, CH), 3.93 (s, 3H, OMe), 3.73 (s, 3H, OMe); for 4a, 10.63 (s, 1H, CH), 7.67 (s, 1H, CH), 7.28 (s, 1H, CH), 4.03 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 3.77 (s, 3H, CH_3); for 4b, 10.00 (s, 1H, CH), 7.62 (s, 1H, CH), 6.68 (s, 1H, CH), 3.98 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 3.77 (s, 3H, CH_3). Anal. Calcd (found) for 3 ($Re_2C_{17}H_8O_{13}$): C, 25.76 (26.35); H, 1.01 (1.01). Calcd (found) for 4a ($Re_2C_{20}H_{12}O_{14}$): C, 28.30 (28.75); H, 1.42 (1.64).

Table I

time, days	amt, % 4a	amt, % 4b	time, days	amt, % 4a	amt, % 4b
0	100	0	4	53	47
1	73	27	6	52	48
2	64	36	7	50	50
3	56	44	9	49	51

Table II

time, days	amt, % 4a	amt, % 4b	time, days	amt, % 4a	amt, % 4b
0	38	62	2	48	52
1	45	55	3	48	52

Reaction of $(OC)_4Re$[*trans*-μ-$HC{=}C(CO_2Me)$]$Re(CO)_4(MeCN)$ (2) with $HC{\equiv}CCO_2Me$ in the Absence of CO. (1) At 25 °C. A 40-mg amount (0.055 mmol) of 2 in 30 mL of CH_2Cl_2 was allowed to react with a 40-μL amount (0.500 mmol) of $HC{\equiv}CCO_2Me$ at 25 °C for 20 h. After the solvent was evaporated at room temperature, the residue was separated by TLC using a 1/2 CH_2Cl_2/hexane solvent mixture to give 27.0 mg of yellow $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (4; 57% yield; a mixture of two isomers) and 1.9 mg of colorless $Re(CO)_4[C_6H_2(CO_2Me)(CO_2Me)_2]$ (5; 6% yield). IR (ν_{CO}, in hexane, cm^{-1}) for 5: 2102 (w), 2001 (s), 1988 (m), 1950 (m), 1735 (w), 1616 (w). ^1H NMR (δ, in acetone-d_6) for 5: 8.40 (d, $^4J_{H-H}$ = 1.7 Hz, 1H, CH), 8.31 (d, $^4J_{H-H}$ = 1.7 Hz, 1H, CH), 4.16 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 3.92 (s, 3H, CH_3). Anal. Calcd (found) for 5 ($ReC_{16}H_{11}O_{10}$): C, 34.97 (35.06); H, 2.00 (2.00).

(2) At 40 °C. When this reaction was conducted in refluxing CH_2Cl_2 for 40 min, separation by TLC gave the following compounds: 3.5 mg of $Re_2(CO)_7[C(CO_2Me){=}C(H)C(CO_2Me){=}C(H)]$ (6; 9% yield), 17.0 mg of 4 (mixture of isomers 4a and 4b; 36% yield), and 2.0 mg of 5 (7% yield). IR (ν_{CO}, in hexane, cm^{-1}) for 6: 2103 (m), 2051 (s), 2030 (m), 1991 (s), 1977 (m), 1960 (m), 1947 (w), 1747 (w), 1740 (w, sh), 1719 (w). ^1H NMR (δ, in $CDCl_3$) for 6: 8.20 (d, $^4J_{H-H}$ = 1.9 Hz, 1H, CH), 7.71 (d, $^4J_{H-H}$ = 1.9 Hz, 1H, CH), 3.87 (s, 3H, OMe), 3.75 (s, 3H, OMe). The mass spectrum of 6 showed the parent ion *m/e* 736 and ions corresponding to the loss of each of the seven carbonyl ligands. Anal. Calcd (found): C, 24.46 (24.47); H, 1.09 (0.95).

Preparation of $Re(CO)_4[C_6H_2(CO_2Me)(CO_2Me)_2]$ (5) from $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (4a). A 10-mg amount (0.012 mmol) of 4a in 20 mL of heptane was heated to reflux for 90 min. After it was cooled, the solution was evaporated to dryness. The residue was separated by TLC using a 1/2 CH_2Cl_2/hexane solvent mixture to give the following bands in order of elution: 0.8 mg of $Re_2(CO)_{10}$, 1.4 mg of 4 (a mixture of isomers 4a and 4b), and 1.4 mg of $Re(CO)_4[C_6H_2(CO_2Me)(CO_2Me)_2]$ (5; 22% yield).

The ^1H NMR spectrum of the reaction residue before chromatography showed a hydride compound (δ −5.80 ppm in acetone-d_6) was formed during the reaction. This hydride compound decomposed during attempts to isolate it by TLC.

Interconversions between 4a and 4b. A deuterated benzene (0.8 mL) solution of 4a (3.0 mg) was added to a 5-mm NMR tube. The progress of conversion of 4a to 4b at 25 °C was monitored regularly by ^1H NMR spectroscopy over a period of 9 days. The results of this analysis are listed in Table I.

Since it is impossible to obtain 4b in pure form, a 3.0-mg amount of a mixture containing 62% of 4b and 38% of 4a in 0.8 mL of deuterated benzene was used to verify the process of conversion of 4b to 4a at 25 °C. The results of this analysis are listed in Table II.

Reaction of 3 with Me_3NO in the Presence of $HC{\equiv}CCO_2Me$. A 10-mg amount (0.013 mmol) of 3 was dissolved in 10 mL of MeCN. A 1.0-mg amount (0.014 mmol) of Me_3NO was added to the above solution. After the solution was stirred at 25 °C for 30 min, the solvent was evaporated under a stream of nitrogen.

Table III. Crystallographic Data for Compounds 3, 4a, and 5

	3	4a	5
empirical formula	$Re_2O_{13}C_{17}H_8$	$Re_2O_{14}C_{20}H_{12}$	$ReO_{10}C_{16}H_{11}$
fw	792.66	848.72	549.46
cryst syst	triclinic	triclinic	triclinic
lattice params			
a (Å)	13.792(2)	10.7738(8)	9.947(1)
b (Å)	14.009(2)	13.179(2)	11.840(2)
c (Å)	6.2734(6)	9.024(1)	7.977(1)
α (deg)	91.47(1)	96.52(1)	106.99(1)
β (deg)	92.95(1)	101.467(8)	102.98(1)
γ (deg)	114.764(8)	84.604(9)	89.52(1)
V (Å^3)	1097.7(2)	1244.2(2)	873.8(2)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	2	2
D_{calc} (g/cm^3)	2.40	2.27	2.09
F_{000}	728	788	524
μ(Mo Kα) (cm^{-1})	112.3	99.2	71.0
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	42.0	44.0	44.0
no. of observns ($I > 3\sigma(I)$)	2120	2428	1968
no. of variables	315	337	252
residuals: R; R_w	0.023; 0.028	0.024; 0.025	0.022; 0.025
goodness-of-fit indicator	1.99	1.39	1.52
max shift in final cycle	0.02	0.00	0.01
largest peak in final diff map (eÅ^3)	0.42	0.59	0.94
abs cor	empirical	empirical	empirical
max/min	1.00/0.35	1.00/0.43	1.00/0.40

The pale yellow residue was redissolved in 15 mL of CH_2Cl_2, and a 10-μL (0.125-mmol) amount of $HC{\equiv}CCO_2Me$ was added to the solution. The above solution was heated to reflux for 3 h and then cooled and evaporated to dryness. Separation of the residue by TLC using a 1/1 CH_2Cl_2/hexane solvent mixture gave 0.5 mg of starting material, 2.8 mg of **6** (30% yield), 3.5 mg of $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (mixture of isomers **4a** and **4b**; 33% yield), and a trace of **5**.

Conversion of $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$ (3) to $Re_2(CO)_7[C(CO_2Me){=}C(H)C(CO_2Me){=}C(H)]$ (6). A 10-mg amount (0.013 mmol) of **3** in 10 mL of MeCN was allowed to react with a 1.0-mg amount (0.014 mmol) of Me_3NO at 25 °C for 30 min. After the solvent was removed in the same way as described above, the residue was redissolved in 15 mL of CH_2Cl_2, the solution was heated to reflux for 3 h and cooled, and the solvent was evaporated. The residue was separated by TLC using a 1/1 CH_2Cl_2/hexane solvent mixture to give 4.7 mg of **6** (50% yield).

Crystallographic Analyses. Pale yellow crystals of **3** were grown from a CH_2Cl_2/hexane solvent mixture by cooling to −3 °C. Pale yellow crystals of **4a** suitable for X-ray diffraction analysis were grown from solution in Et_2O solvent by cooling to −14 °C. Colorless crystals of **5** were grown from a solution in hexane/CH_2Cl_2/MeOH solvent by cooling to −3 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table III. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o|-|F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

All three compounds crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solutions and refinements of the structures. All three structures were solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL). All non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters.

For compound **3** the hydrogen atoms H(1) and H(3) were located and refined using isotropic thermal parameters. The positions of the hydrogen atoms on the methyl groups were calculated by assuming idealized geometries. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

For compound **4a** the hydrogen atoms H(3), H(4), and H(7) were located and refined using isotropic thermal parameters. The positions of the hydrogen atoms on the methyl groups were calculated by assuming idealized geometries. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

For compound **5** the hydrogen atoms H(3) and H(5) were located and refined using isotropic thermal parameters. The positions of the hydrogen atoms on the methyl groups were calculated by assuming idealized geometries. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

The reaction of $(OC)_4Re[$*trans*-μ-$HC{=}C(CO_2Me)]Re(CO)_5$ (**1**) with Me_3NO in MeCN solvent yielded the acetonitrile derivative $(OC)_4Re[$*trans*-μ-$HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ (**2**) in 71% yield. It is believed that the substitution occurred at the CO-rich $Re(CO)_5$ group in **1**. This was not experimentally established in this study, but it is fully consistent with the products obtained from the reactions of **2** with $HC{\equiv}CCO_2Me$ (see below). When complex **2** was allowed to react with $HC{\equiv}CCO_2Me$ in refluxing CH_2Cl_2 under an atmosphere of CO, the two new complexes $(OC)_4Re[\mu$-$C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$ (**3**; 11%) and $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (**4a,b**; 49%) were formed. Compound **4** exists in solution as a mixture of two isomers. One of these, **4a**, was obtained in a pure form by crystallization. As expected when this reaction was performed in the absence of CO, no **3** was formed, and the yield of compounds **4a,b** was increased (57%), but a small amount of the new compound $Re(CO)_4[C_6H_2(CO_2Me)(CO_2Me)_2]$ (**5**; 6%) was obtained at 25 °C. A similar result was obtained at 40 °C, but still another new compound, $Re_2(CO)_7[C(CO_2Me){=}C(H)C(CO_2Me){=}C(H)]$ (**6**), was formed in low yield (9%). The molecular formula of compound **6** was established from its mass spectrum. The similarity of its IR spectrum to those for metallacyclic compounds obtained from the reaction of $Re_2(CO)_8(\mu$-$MeCCNMe_2)$ with $MeC{\equiv}CNMe_2$ (eq 1) suggests that it too has a similar metallacyclic structure. The observation of two OMe and two CH resonances indicates that **6** is the isomer formed by the head-to-tail coupling of the two $HC{\equiv}CCO_2Me$ molecules.

When **3** was decarboxylated by Me_3NO, it was converted into **6** in 50% yield. Complex **3** was converted into the

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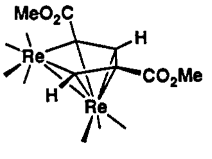
[9] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IX, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.



6

mixture of **4a,b** in 33% yield by reaction with Me_3NO in the presence of $HC{\equiv}CCO_2Me$, but a significant amount of **6** was still formed (30% yield). Compound **5** was obtained in 22% yield from **4a** when heated to 98 °C. Three of the products **3**, **4a**, and **5** were characterized by single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of **3** is shown in Figure 1. Final fractional atomic coordinates are listed in Table IV. Compound **3** contains two metal-containing groupings that are linked by a four-carbon chain which was formed by the head-to-tail coupling of two $HC{\equiv}CCO_2Me$ molecules. The CH terminus of the chain is σ-bonded to Re(2) (Re(2)–C(1) = 2.166(9) Å). The $C(CO_2Me)$ terminus is σ-bonded to Re(1) (Re(1)–C(4) = 2.232(8) Å). There is a C–C double bond between carbons C(1) and C(2) and C(3) and C(4) (C(1)–C(2) = C(3)–C(4) = 1.33(1) Å). The carboxylate group bonded to C(2) is coordinated to the rhenium atom, Re(2), by the ketonic oxygen atom to form a metallacycle (Re(2)–O(1) = 2.187(5) Å). A similarly structured metallacycle was shown to exist in compound **1**.[8] The alkenyl hydrogen atoms were located and refined crystallographically and show the expected deshielded shifts in the ^1H NMR spectrum (δ 9.62, 7.66 ppm) with long-range coupling ($^4J_{H-H}$ = 1.5 Hz).

An ORTEP diagram of the molecular structure of **4a** is shown in Figure 2. Final fractional atomic coordinates are listed in Table V. The two metal-containing groups in **4a** are linked by a six-carbon chain that was formed by the head-to-tail coupling of three $HC{\equiv}CCO_2Me$ molecules. The CH terminus of the chain is σ-bonded to Re(1) (Re(1)–C(3) = 2.143(8) Å). The $C(CO_2Me)$ terminus is σ-bonded to Re(2) (Re(2)–C(8) = 2.194(8) Å). There are C–C double bonds between carbons C(2) and C(3), C(4) and C(5), and C(7) and C(8): C(2)–C(3) = 1.36(1) Å, C(4)–C(5) = 1.35(1) Å, and C(7)–C(8) = 1.32(1) Å. As in **3**, the carboxylate group bonded to C(2) is coordinated to the rhenium atom, Re(1), by the ketonic oxygen atom to form a metallacycle (Re(1)–O(1) = 2.187(6) Å), but in addition the ketonic oxygen on the carboxylate group at carbon C(5) is coordinated to the other metal atom to form a six-membered metallacyclic ring (Re(2)–O(3) = 2.161(6) Å). The three alkenyl hydrogen atoms for **4a** show the expected deshielded shifts in the ^1H NMR spectrum (δ 10.63 (s), 7.67 (s), and 7.28 (s) ppm). In solution three new alkenyl hydrogen resonances (δ 10.00 (s), 7.62 (s), and 6.68 (s) ppm) and three new OMe resonances appeared and grew in intensity over a period of days. These are attributed to the isomer **4b**. At equilibrium the **4a**/**4b** ratio was 49/51.

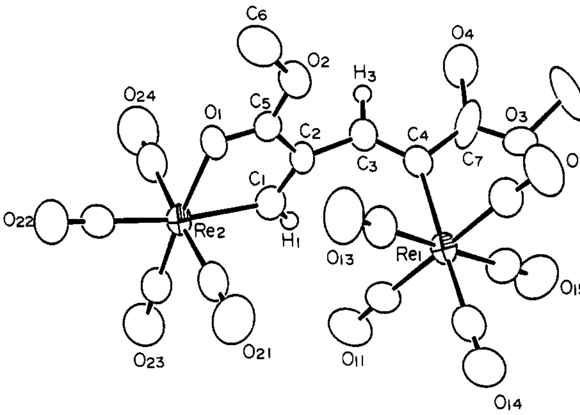


Figure 1. ORTEP diagram of $(OC)_4Re[\mu\text{-}C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$ (**3**), showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) are as follows: Re(1)–C(4) = 2.232(8), Re(2)–C(1) = 2.169(9), Re(2)–O(1) = 2.187(5), C(1)–C(2) = 1.33(1), C(2)–C(5) = 1.45(1), C(2)–C(3) = 1.48(1), C(3)–C(4) = 1.33(1), C(4)–C(7) = 1.51(1).

Table IV. Positional Parameters and *B*(eq) Values for $Re_2(CO)_9(HCCCO_2Me)_2$ (3)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	0.66621(02)	0.39912(02)	0.24286(05)	3.25(2)
Re(2)	0.94903(02)	0.18611(02)	0.25784(06)	3.57(2)
O(1)	0.8069(04)	0.0943(04)	0.4264(09)	3.9(2)
O(2)	0.6317(05)	0.0477(05)	0.4359(09)	4.7(3)
O(3)	0.4407(19)	0.2688(13)	−0.034(04)	5(1)
O(4)	0.4177(12)	0.1091(11)	−0.082(03)	8.3(8)
O(5)	0.4896(12)	0.2157(18)	−0.256(03)	10(1)
O(6)	0.4172(17)	0.223(03)	0.037(03)	7(1)
O(11)	0.8815(06)	0.4567(05)	0.0249(13)	7.2(4)
O(12)	0.4479(06)	0.3479(07)	0.4472(12)	7.4(4)
O(13)	0.7406(07)	0.2991(06)	0.6204(12)	7.3(4)
O(14)	0.7622(06)	0.6178(06)	0.4885(13)	6.9(3)
O(15)	0.5935(06)	0.4917(05)	−0.1458(12)	6.9(3)
O(21)	1.0016(07)	0.3885(07)	0.5471(16)	9.2(5)
O(22)	1.0987(06)	0.1208(06)	0.5506(13)	7.2(4)
O(23)	1.1310(06)	0.3191(06)	−0.0105(13)	7.5(4)
O(24)	0.8928(06)	0.0028(07)	−0.0853(14)	7.9(4)
C(1)	0.8200(07)	0.2113(06)	0.0950(14)	3.9(4)
C(2)	0.7238(06)	0.1634(06)	0.1715(13)	3.5(3)
C(3)	0.6217(07)	0.1618(07)	0.0810(14)	3.8(3)
C(4)	0.5901(06)	0.2394(06)	0.0777(12)	3.3(3)
C(5)	0.7232(07)	0.1000(06)	0.3511(14)	3.6(3)
C(6)	0.6300(08)	−0.0181(08)	0.6106(16)	6.1(4)
C(7)	0.4832(11)	0.2075(09)	−0.044(02)	6.0(6)
C(8)	0.3226(08)	0.2212(11)	−0.098(02)	8.9(7)
C(11)	0.8032(08)	0.4335(07)	0.1037(16)	4.9(4)
C(12)	0.5273(08)	0.3637(07)	0.3729(14)	4.5(4)
C(13)	0.1732(08)	0.3342(08)	0.4835(15)	4.7(4)
C(14)	0.7275(07)	0.5373(08)	0.3986(16)	4.7(4)
C(15)	0.6180(07)	0.4572(07)	−0.0030(15)	4.2(4)
C(21)	0.9810(08)	0.3127(08)	0.4484(19)	5.7(5)
C(22)	1.0446(07)	0.1444(07)	0.4428(16)	4.7(4)
C(23)	1.0635(07)	0.2692(07)	0.0925(16)	4.8(4)
C(24)	0.9137(07)	0.0684(08)	0.0434(17)	4.9(4)

An ORTEP diagram of the molecular structure of **5** is shown in Figure 3. Final fractional atomic coordinates are listed in Table VI. Compound **5** contains only one metal atom, which has four linear terminal carbonyl ligands. The most interesting ligand is a 2,4,6-tris(methoxycarbonyl)phenyl group that is σ-bonded to the metal atom (Re(1)–C(1) = 2.194(6) Å). One of the carboxylate groups is coordinated to the rhenium atom by the ketonic oxygen atom to form a metallacycle (Re(1)–O(1) = 2.02(1) Å). Due to the coordination of one of the carboxylate groups, the hydrogen atoms on the phenyl group are structurally inequivalent. This inequivalence is observed in the ^1H NMR spectrum by two resonances (δ 8.40 (d) and 8.31 (d) ppm) with long-range coupling ($^4J_{H-H}$ = 1.7 Hz).

A summary of the results of this study is shown in Scheme I. When compound **1** was transformed into the activated acetonitrile derivative **2**, it readily reacted (40 °C) with $HC{\equiv}CCO_2Me$ at the carboxylate-substituted Re–C bond. We note that **1** itself does not react with $HC{\equiv}CCO_2Me$ at temperatures less than 98 °C. Thus, it

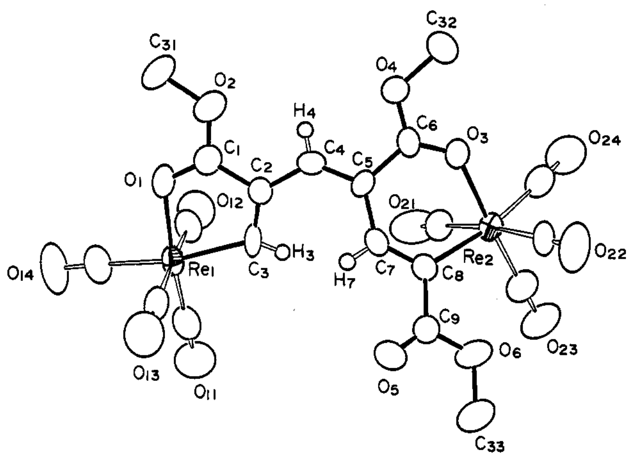


Figure 2. ORTEP diagram of $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (**4a**). Selected interatomic distances (Å) are as follows: Re(1)–C(3) = 2.143(8), Re(2)–C(8) = 2.194(8), Re(1)–O(1) = 2.187(6), Re(2)–O(3) = 2.161(6), C(1)–C(2) = 1.47(1), C(2)–C(3) = 1.36(1), C(2)–C(4) = 1.45(1), C(4)–C(5) = 1.35(1), C(5)–C(6) = 1.48(1), C(5)–C(7) = 1.46(1), C(7)–C(8) = 1.32(1), C(8)–C(9) = 1.51(1).

Table V. Positional Parameters and *B*(eq) Values for $Re_2(CO)_8(HCCCO_2Me)_3$ (4a)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	0.21800(03)	0.44017(03)	0.32082(04)	3.36(2)
Re(2)	0.18473(03)	–0.08256(03)	–0.23439(04)	3.55(2)
O(1)	0.2968(05)	0.5001(04)	0.1458(07)	3.9(3)
O(2)	0.3421(05)	0.4662(04)	–0.0873(07)	4.4(3)
O(3)	0.2627(05)	0.0295(05)	–0.3402(06)	4.1(3)
O(4)	0.3299(06)	0.1750(05)	–0.3810(07)	4.8(3)
O(5)	0.4169(08)	–0.0230(05)	0.2256(07)	6.6(4)
O(6)	0.3125(06)	–0.1545(05)	0.1019(07)	5.4(3)
O(11)	0.0951(07)	0.3423(07)	0.5411(09)	7.6(5)
O(12)	–0.0574(07)	0.4976(06)	0.1515(09)	7.4(4)
O(13)	0.4811(06)	0.3774(06)	0.5174(09)	6.8(4)
O(14)	0.2182(07)	0.6475(06)	0.5232(09)	8.1(4)
O(21)	–0.0450(09)	0.0616(08)	–0.1585(10)	10.1(6)
O(22)	0.4276(06)	–0.2285(05)	–0.2522(09)	6.2(4)
O(23)	0.0762(07)	–0.2497(06)	–0.0995(09)	6.8(4)
O(24)	0.0335(08)	–0.1531(06)	–0.5547(09)	9.0(5)
C(1)	0.3058(07)	0.4382(07)	0.0333(10)	3.4(4)
C(2)	0.2760(07)	0.3313(06)	0.0275(09)	3.1(4)
C(3)	0.2326(07)	0.3133(06)	0.1527(10)	3.3(4)
C(4)	0.2857(08)	0.2640(07)	–0.1094(10)	3.6(4)
C(5)	0.2968(07)	0.1608(06)	–0.1332(09)	3.3(4)
C(6)	0.2943(08)	0.1163(07)	–0.2914(09)	3.6(4)
C(7)	0.3209(09)	0.0905(07)	–0.0156(10)	3.8(4)
C(8)	0.2953(08)	–0.0066(07)	–0.0278(09)	3.5(4)
C(9)	0.3469(09)	–0.0589(07)	0.1146(10)	4.0(4)
C(11)	0.1424(08)	0.3797(08)	0.4571(11)	4.6(5)
C(12)	0.0443(10)	0.4770(07)	0.2096(11)	5.0(5)
C(13)	0.3875(08)	0.3992(07)	0.4401(10)	4.0(4)
C(14)	0.2173(08)	0.5725(08)	0.4464(11)	4.9(5)
C(21)	0.0382(10)	0.0137(08)	–0.1877(11)	5.2(5)
C(22)	0.3393(09)	–0.1771(07)	–0.2502(10)	4.1(4)
C(23)	0.1174(08)	–0.1861(08)	–0.1497(11)	4.7(5)
C(24)	0.0898(10)	–0.1290(08)	–0.4361(13)	5.3(5)
C(31)	0.3577(09)	0.5740(07)	–0.0898(12)	5.3(5)
C(32)	0.3371(12)	0.1288(08)	–0.5333(11)	6.6(6)
C(33)	0.3433(11)	–0.2057(08)	0.2387(12)	6.7(6)

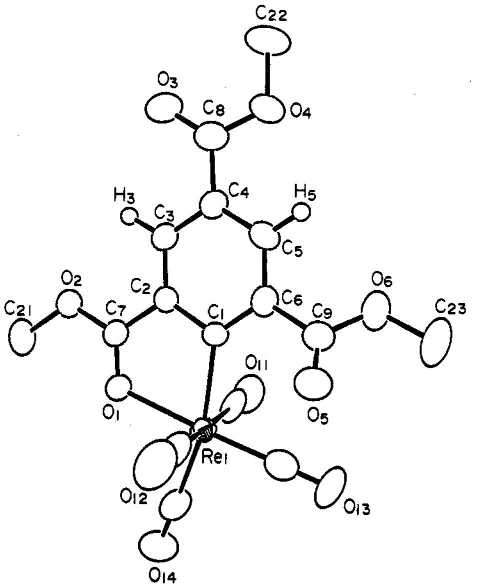


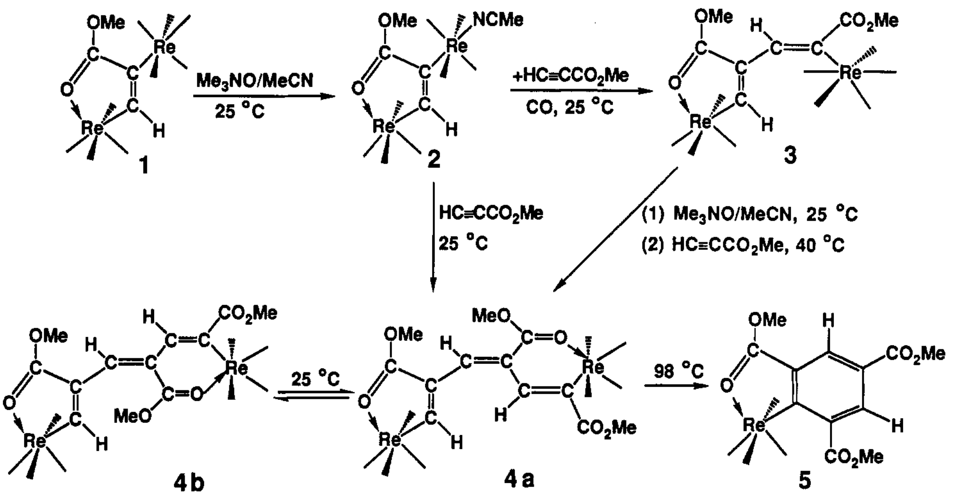
Figure 3. ORTEP diagram of $\overline{Re(CO)_4[C_6H_2(C}O_2Me)(CO_2Me)_2]$ (**5**), showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–O(1) = 2.02(1), Re(1)–C(1) = 2.194(6), C(1)–C(2) = 1.402(8), C(2)–C(3) = 1.380(9), C(3)–C(4) = 1.380(9), C(4)–C(5) = 1.385(9), C(5)–C(6) = 1.39(1), C(1)–C(6) = 1.410(9); O(1)–Re(1)–C(1) = 76.1(2).

Table VI. Positional Parameters and *B*(eq) Values for $Re(CO)_4[C_6H_2(CO_2Me)_3]$ (5)

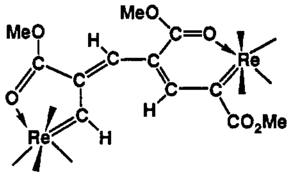
atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	–0.05160(03)	0.19381(02)	–0.11582(03)	2.46(1)
O(1)	0.0734(04)	0.2648(04)	–0.2618(06)	2.8(2)
O(2)	0.0664(04)	0.3454(04)	–0.4836(06)	3.1(2)
O(3)	–0.3902(06)	0.3986(05)	–0.8542(07)	5.7(3)
O(4)	–0.5739(05)	0.3854(05)	–0.7415(07)	5.0(2)
O(5)	–0.3816(05)	0.0384(05)	–0.3065(08)	4.9(2)
O(6)	–0.5405(06)	0.1734(05)	–0.2813(07)	5.0(2)
O(11)	–0.0735(06)	0.4497(05)	0.1274(07)	5.1(2)
O(12)	–0.0580(06)	–0.0627(05)	–0.3770(07)	5.6(3)
O(13)	–0.2321(06)	0.1036(05)	0.0900(07)	5.0(2)
O(14)	0.2149(06)	0.1638(05)	0.1525(07)	5.0(2)
C(1)	–0.2053(07)	0.2323(05)	–0.3333(08)	2.6(2)
C(2)	–0.1456(06)	0.2913(05)	–0.4301(08)	2.5(2)
C(3)	–0.2213(07)	0.3344(06)	–0.5631(09)	2.8(3)
C(4)	–0.3635(07)	0.3204(06)	–0.6065(08)	3.1(3)
C(5)	–0.4277(07)	0.2581(06)	–0.5207(09)	3.3(3)
C(6)	–0.3503(07)	0.2132(06)	–0.3898(09)	3.1(3)
C(7)	0.0065(07)	0.3000(05)	–0.3850(08)	2.6(2)
C(8)	–0.4419(08)	0.3702(06)	–0.7484(10)	3.8(3)
C(9)	–0.4219(07)	0.1319(07)	–0.3205(09)	3.7(3)
C(11)	–0.0656(08)	0.3579(06)	0.0396(09)	3.6(3)
C(12)	–0.0554(08)	0.0308(07)	–0.2825(09)	3.9(3)
C(13)	–0.1652(08)	0.1362(06)	0.0094(09)	3.4(3)
C(14)	0.1151(08)	0.1725(06)	0.0533(09)	3.4(3)
C(21)	0.2160(08)	0.3488(07)	–0.4412(10)	4.2(3)
C(22)	–0.6544(09)	0.4371(08)	–0.8723(12)	6.1(4)
C(23)	–0.6201(10)	0.0938(09)	–0.2211(13)	6.7(4)

seems most likely that the first step in the reaction is a coordination of HC≡CCO_2Me by displacement of the MeCN ligand. Since the CO ligands in **1** are more strongly coordinated than the MeCN ligand in **2**, the reaction cannot get started. Once the alkyne is coordinated, the relatively facile head-to-tail C–C coupling takes place with the alkyne that lies between the two rhenium atoms. This transformation would produce a vacant coordination site at the rhenium atom where the insertion took place, and when the reaction was performed under a CO atmosphere, a CO ligand was added at that vacant site and the stable product **3** was formed. However, in the absence of CO a second molecule of HC≡CCO_2Me was added with insertion into the metal–carbon bond to produce the compound **4a** by the head-to-tail coupling of the three alkynes. One of the carboxylate ligands then became coordinated at the vacant site, and **4a** was stabilized sufficiently so that further alkyne addition and coupling did occur under these conditions. The compounds **4** exist as two isomers in

Scheme I



solution. One of these, **4a**, was isolated and characterized crystallographically. It has an *E* geometry at the C–C double bond (C(4)–C(5); see Figure 2). It is proposed that the structure of **4b** is similar to that of **4a** but has simply the *Z* geometry at the C(4)–C(5) double bond (cf. Scheme I). If this is true, then an explanation for the facile isomerization at 25 °C is required. We believe that this could be explained by a substantial contribution of the resonance structure B, in which the two metal–carbon bonds would have carbene character. As a result, the C–C double bond at C(4)–C(5) would become single and a rotation of 180° about the bond would interchange the isomers.



B

The cyclization transformation of 4 that forms the aryl ring in **5** is an unusual one. It requires a cleavage of the C–H bond at the carbon labeled C(3) in Figure 2 and a coupling to the carbon C(8). The C–H bond cleavage is probably a metal-activated process. This could be accomplished by a decoordination of the carboxylate group on Re(2) to provide a vacant coordination site. If this occurred in the isomer **4a**, a subsequent rotation about the C(5)–C(7) single bond would bring the Re(2) proximate to the C–H bond on C(3). After the insertion of Re(2) into the C(3)–H(3) bond, both C(3) and C(8) would be coordinated to Re(2). A reductive elimination of carbons C(3) and C(8) would complete the aromatization and result in expulsion of a hydride-containing rhenium carbonyl grouping. We have searched for hydride-containing metal fragments and have observed a hydride resonance at δ −5.80 ppm in reaction mixtures analyzed by ^{1}H NMR spectroscopy. This resonance position is close to that of HRe(CO)$_5$,[10] but we were unable to isolate the compound due to decomposition during chromatography and its identification was not confirmed. It is possible that it might be some reactive-solvated species such as HRe(CO)$_4$(Sol). A search for $H_3Re_3(CO)_{12}$ was negative.

This study has shown that suitably activated rhenium carbonyl groupings readily produce head-to-tail oligomerization of HC≡CCO$_2$Me under very mild conditions, resulting in novel cyclization transformation yielding a σ-coordinated trisubstituted aryl ring.

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Supplementary Material Available: Tables of hydrogen atom positional parameters, bond distances and angles, and anisotropic thermal parameters for all three structural analyses (18 pages). Ordering information is given on any current masthead page.

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[10] Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1978**, *152*, 85.