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Synthesis and Reactivity of (η^6-arene)tricarbonylchromium Compounds Incorporating Propargylamine Units. X-ray Crystal Structures of $YCH_2C{\equiv}CPh[Cr(CO)_3]$ (Y = NMe_2, $N(Me)(CH_2Ph)$) and {Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(Cl)(Py)$}

Elton L. S. Gomes,[⊥] Manfredo Hörner,[§] Victor G. Young, Jr.,[†] Jairton Dupont,[⊥]
Vinicius Caliman,[‡] and Osvaldo L. Casagrande, Jr.*,[⊥]

Laboratório de Catálise Molecular, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre, RS, 91509-900, Brazil, Departamento de Química−ICEx, UFMG, Belo Horizonte, MG, 31270-901, Brazil, Departamento de Química, UFSM, Santa Maria, RS, 97105-900, Brazil, and Department of Chemistry, The University of Minnesota, Minneapolis, Minnesota 55455

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The syntheses, structures, and reactivities of new (η^6-arene)tricarbonylchromium compounds bearing propargylamines are described. The reaction of (η^6-C_6H_5Cl)tricarbonylchromium with propargylamines affords $YCH(R)C{\equiv}CPh[Cr(CO)_3]$ (**1a**, R = H, Y = NMe_2; **1b**, R = Me, Y = NMe_2; **1c**, R = H, Y = $N(Me)(CH_2Ph)$) in good yield. The reaction of **1a**,**b** with Li_2PdCl_4 generates the air-stable dimeric compounds {Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH(R)NMe_2$-($\mu$-Cl)}$_2$ (**2a**, R = H; **2b**, R = Me), which can be converted to a monomeric and soluble species {Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH(R)NMe_2(Cl)(Py)$} (**3a**, R = H; **3b**, R = Me) after reaction with pyridine. Compounds **1a**, **1c**, and **3a** were structurally characterized by single-crystal X-ray diffraction studies.

Introduction

It is well-known that the presence of the $Cr(CO)_3$ unit induces an electron-deficient character on the phenyl ring, and consequently several useful organic and organometallic reactions have been facilitated.[1] In recent years, much attention has been focused on the synthesis of heterometallic complexes derived from (η^6-arene)-tricarbonylchromium fragments especially due to their singular structural and electronic properties.[2] In particular, Pfeffer's group has recently shown that the cyclomanganated (η^6-arene)tricarbonylchromium complexes display a unique reactivity toward alkynes and nucleophiles.[2b−d] It is interesting to note that although cyclopalladated compounds are by far the most investigated family among “classical” cyclometalated complexes, cyclopalladated (η^6-arene)tricarbonylchromium complexes are not known. This can be probably associated with the methods generally employed in the synthesis of cyclopalladated complexes, i.e., C−H bond activation (cyclopalladation) and transmetalation reactions.[3] In fact, initial attempts to perform the cyclopalladation of either [{η^6-$C_6H_5CH_2N(CH_3)_2$}$Cr(CO)_3$] or [(η^6-$C_6H_5C_5H_5N$)$Cr(CO)_3$] derivatives using these methods have failed, and only decomposition products resulting from redox reactions have been observed. Nevertheless, it should be pointed out that stable bimetallic complexes containing Cr−Pd[4] or aryl−pal-

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* To whom correspondence should be addressed. E-mail: osvaldo@if.ufrgs.br.

[§] Universidade Federal de Santa Maria.

[†] The University of Minnesota.

[‡] Universidade Federal de Minas Gerais.

[⊥] Universidade Federal do Rio Grande do Sul.

[1] (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; Chapter 10. (b) Davies, S. G. In *Organotransition Metal Chemistry, Applications to Organic Syntheses*; Pergamon Press: Oxford, U.K., 1982; p 166. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Vol. 20, p 921. (d) Merlic, C. A.; Walsh, J. C. *Tetrahedron Lett.* **1998**, *39*, 2083. (e) Ariffin, A.; Blake, A. J.; Li, W.-S.; Simpkins, N. S. *Synlett* **1997**, 1453. (f) Cowton, E. L. M.; Gibson, S. E.; Schneider, M. J.; Smith, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 839. (g) Küding, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (h) Kalinin, V. N. *Russ. Chem. Rev.* **1987**, *56*, 682. (i) Oishi, T.; Fukui, M.; Endo, Y. *Heterocycles* **1977**, *7*, 947. (j) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7091. (k) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7092.

[2] (a) Clark, G. R.; Metzler, M. R.; Whitaker, G.; Woodgate, P. D. *J. Organomet. Chem.* **1996**, *513*, 109. (b) Djukic, J. P.; Maisse, A.; Pfeffer, M. *Organometallics* **1997**, *16*, 657. (c) Djukic, J. P.; Maisse, A.; Pfeffer, M.; Dötz, K. H.; Nieger, M. *Eur. J. Inorg. Chem.* **1998**, 1781. (d) Djukic, J. P.; Maisse, A.; Pfeffer, M. *J. Organomet. Chem.* **1998**, *567*, 65. (e) Hunter, A. D.; Ristic-Petrovic, D.; McLernon, J. L. *Organometallics* **1992**, *11*, 864. (f) Li, J.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D.; Bott, S. G.; Atwood, J. L. *Organometallics* **1992**, *11*, 3050.

[3] Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759, and references therein.

[4] (a) Moiseev, S. K.; Cherepanov, I. A.; Petrovskii, P. V.; Ezernitskaya, M. G.; Butenschon, H.; Strotmann, M.; Kalinin, V. N. *Inorg. Chim. Acta* **1998**, *1−2*, 71. (b) Kalinin, V. N.; Cherepanov, I. A.; Moiseev, S. K.; Batsanov, A. S.; Struchkov, Yu. T. *Mendeleev. Commun.* **1991**, 77.

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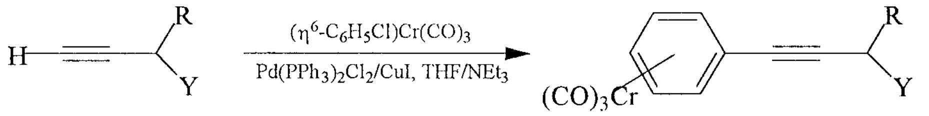
Scheme 1



1a: R = H; Y = NMe$_2$
1b: R = Me; Y = NMe$_2$
1c: R = H; Y = N(Me)(CH$_2$Ph)

ladium bonds[5] have been synthesized.

We have recently shown that the chloropalladation reaction of propargylamines and thioethers are a simple and facile method for the preparation of a series of cyclopalladated compounds.[6] We anticipate that this method can be extended to the synthesis of heterobimetallic cyclopalladated complexes derived from (η^6-arene)tricarbonylchromium compounds. We report herein the synthesis and characterization of (η^6-arene)tricarbonylchromium complexes incorporating propargylamine units and their use as starting materials to obtain novel heterobimetallic cyclopalladated compounds.

Results and Discussion

Synthesis of (η^6-arene)tricarbonylchromium Complexes Bearing Propargylamine Moieties. The preparative procedure for (η^6-arene)tricarbonylchromium complexes bearing propargylamine fragments was analogous to the literature.[7] Thus, reaction of (η^6-C_6H_5Cl)tricarbonylchromium complex with 1.5 equiv of propargylamines in the presence of a catalytic amount of $Pd(PPh_3)_2Cl_2$/CuI in gently refluxing THF/NEt$_3$ afforded the complexes YCH(R)C≡CPh[Cr(CO)$_3$] (**1a**, R = H, Y = NMe$_2$; **1b**, R = Me, Y = NMe$_2$; **1c**, R = H, Y = N(Me)CH$_2$Ph), respectively (Scheme 1).

The resulting arene tricarbonyl chromium complexes **1a**–**c** are air-stable and can be isolated in good yields (70–75%) as yellow or orange solids after purification by chromatography column. The structures of **1a**–**c** were assigned on the basis of elemental analysis, MS, IR, and multinuclear (^{1}H, ^{13}C) NMR data and by the X-ray structural determinations carried out for **1a** and **1c**. The IR spectrum of **1a** shows three bands of the carbonyl stretching frequencies determined by a splitting of the asymmetric mode (E), which can be rationalized in terms of a small perturbation of C_{3v} symmetry by an alkyne fragment on the benzene ring.[8] As expected, the IR spectra of complexes **1b**,**c** in the solid state show two intense bands of the carbonyl stretching frequencies between 2100 and 2000 cm^{-1} as the result of a pseudo C_{3v} symmetry of Cr(CO)$_3$ groups. The lower medium frequency of the CO stretching ($\bar{\nu}$ CO) for **1a** (1914 cm^{-1}) related to those found for **1b** (1922 cm^{-1}) and **1c** (1927 cm^{-1}) reflects a greater negative charge on the Cr(CO)$_3$ moiety, suggesting a better electron donor capacity of the alkyne unit containing a NMe$_2$ group. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1a**–**c** showed the usual upfield shift of the aromatic proton and carbon resonances with respect to those of the corresponding free arenes. These resonances are found in the same region of the spectrum, indicating that there is no electronic influence from the groups present in the propargylamine moieties on the aromatic ring. As expected, the resonances of the alkyne carbons occur in the region between 89 and 85 ppm. The mass spectral data for **1a**–**c** show a similar fragmentation for all compounds (see Experimental Section).

Molecular Structures of YCH$_2$C≡CPh[Cr(CO)$_3$] (1a, Y = NMe$_2$; 1c, Y = N(Me)CH$_2$Ph)). Crystal data for **1a** and **1c** are summarized in Table 1, refinement details are discussed in the Experimental Section, and selected bond distances and angles are listed in Tables 2 and 3. Molecular geometries and atom-labeling schemes are shown in Figures 1 and 2.

The arene tricarbonylchromium complexes **1a** and **1c** crystallize in the triclinic system. In both cases the Cr(CO)$_3$ unit adopts a nearly staggered conformation. The alkyne fragments are found lying in the mean plane of the arene ring, whereas the C$_{ipso}$–C≡C linkage is almost linear (**1a** = 177.7°; **1c** = 179.0°). The C–C triple bond distances in **1a** (1.187 Å) and **1c** (1.189 Å) are in agreement with similar arene tricarbonyl chromium derivatives.[7] The arene ligand did not undergo any significant folding after the incorporation of the alkyne moiety. Furthermore, it can be noticed that the aromatic carbons remain in the mean plane of the arene.

Heterobimetallic Cyclopalladated Complexes. The *trans*-Chloropalladation Reaction of 1a,b Using Li$_2$PdCl$_4$. The reaction of equimolar amounts of **1a**,**b** and Li$_2$PdCl$_4$ (MeOH, −40 °C, Scheme 2) affords the air-stable dimeric species {Pd-*trans*-C[(Ph)Cr(CO)$_3$]=C(Cl)CH(R)NMe$_2$(μ-Cl)}$_2$ (**2a,** R = H; **2b**, R = Me) as a yellow solids in 64–67% yield. The dimeric compounds **2a**,**b** are insoluble in the most common solvents, and therefore their characterization in solution was difficult. Nevertheless, the absence of the ν(C≡C) band at 2233 and 2227 cm^{-1} and the presence of ν(C=C) around 1600 cm^{-1} in the IR spectra of **2a**,**b** suggest the formation of the chlorovinylmetallacycle complex. The carbonyl stretching band patterns of **2a**,**b** are similar to those of **1a**–**c**; that is, they exhibit the same number of bands, indicating that the symmetry around the chromium center remains unchanged.

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[5] (a) Dufaud, V.; Thivolle-Cazat, J.; Basset, J. M.; Mathieu, R.; Jaud, J.; Waissermann, J. *Organometallics* **1991**, *10*, 4005.

[6] (a) Dupont, J.; Casagrande. O. L., Jr., Aiub, A. C.; Beck, J.; Hörner, M.; Bortoluzzi, A. *Polyhedron* **1994**, *13*, 2583. (b) Dupont, J.; Basso, N. R.; Meneghetti, M. R. *Polyhedron* **1996**, *15*, 2299. (c) Dupont, J.; Casagrande. O. L., Jr.; Aiub, A. C.; Basso, N. R.; Mössmer, C. M.; Hörner, M.; Bortoluzzi, A. *J. Coord. Chem.* **1996**, *40*, 35. (d) Dupont, J.; Basso, N. R.; Meneghetti, M. R.; Konrath, R.; Burrow, R.; Hörner, M. *Organometallics* **1997**, *16*, 2386. (e) Dupont, J.; Casagrande. O. L., Jr.; Aiub, A. C.; Beck, J.; Hörner, M. *J. Organomet. Chem.* (manuscript in preparation).

[7] (a) Müller, T. J. J.; Lindner, J. *Chem. Ber.* **1996**, *129*, 607. (b) Müller, T. J. J.; Ansorge, M.; Lindner, J. *Chem. Ber.* **1996**, *129*, 1433. (c) Müller, T. J. J.; Ansorge, M.; Lindner, J. *Chem. Ber.* **1997**, *130*, 1135.

[8] (a) Fisher, R. D. *Chem. Ber.* **1960**, *93*, 165. (b) Brown, D. A.; Raju, J. R. *J. Chem. Soc. A* **1966**, 1617.

Table 1. Summary of Crystallographic Data for 1a, 1c, and 3a·$CHCl_3$

	1a	**1c**	**3a**•$CHCl_3$
formula	$C_{14}H_{13}CrNO_3$	$C_{20}H_{17}CrNO_3$	$C_{20}H_{19}Cl_5CrN_2O_3Pd$
fw	295.25	371.35	671.02
T (K)	293(2)	173(2)	293(2)
cryst system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.193(2)	7.1542(4)	10.659(2)
b (Å)	8.914(2)	9.6422(6)	11.309(2)
c (Å)	11.153(2)	13.6376(8)	11.989(2)
α (deg)	110.85(3)	72.400(2)	93.23(3)
β (deg)	95.92(3)	80.861(2)	115.60(3)
γ (deg)	110.78(3)	86.097(2)	95.43(3)
V (Å^3)	686.7(2)	885.13(9)	1289.8(4)
Z	2	2	2
diffractometer	Enraf-Nonius CAD4	Siemens SMART Platform CCD	Enraf-Nonius CAD4
d (calcd), g cm^{-3}	1.428	1.393	1.728
abs coeff, mm^{-1}	0.835	0.664	1.661
F(000)	304	384	664
cryst size, mm	0.43 × 0.36 × 0.26	0.28 × 0.24 × 0.19	0.43 × 0.33 × 0.30
θ range for data collcn	2.60 to 25.48°	1.58 to 25.05°	2.62 to 25.29°
no. of unique reflcns collcd	2687	5055	4953
no. of obsd data [$I > 2\sigma(I)$]	2547 ($R_{int} = 0.0080$)	3048 ($R_{int} = 0.0289$)	4694 ($R_{int} = 0.0153$)
no. of data/params	2547/212	3048/227	4694/287
goodness-of-fit on F^2	1.047	1.014	1.040
final R indices [$I > 2\sigma(I)$]	R1 = 0.0287, wR2 = 0.0836	R1 = 0.0506, wR2 = 0.1010	R1 = 0.0341, wR2 = 0.0843
$\Delta\rho$ (max,min), e Å^{-3}	0.201, −0.216	0.370, −0.447	0.733, −0.775

[a] Refinement method, full-matrix least-squares on F^2 . [b]Graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a

Cr−C(11)	2.230(2)	Cr−C(41)	1.837(2)
Cr−C(12)	2.214(2)	O(21)−C(21)	1.142(3)
Cr−C(13)	2.208(2)	O(31)−C(31)	1.149(3)
Cr−C(14)	2.213(2)	O(41)−C(41)	1.146(3)
Cr−C(15)	2.209(2)	C(1)−C(2)	1.187(3)
Cr−C(16)	2.217(2)	C(11)−C(1)	1.437(3)
Cr−C(21)	1.848(3)	C(2)−C(3)	1.484(3)
Cr−C(31)	1.838(2)	C(3)−N(4)	1.461(3)
O(21)−C(21)−Cr	179.1(2)	C(21)−Cr−C(31)	88.85(11)
O(31)−C(31)−Cr	179.0(2)	C(41)−Cr−C(21)	88.14(12)
O(41)−C(41)−Cr	179.1(2)	C(1)−C(2)−C(3)	174.6(2)
C(41)−Cr−C(31)	88.34(10)	C(11)−C(1)−C(2)	177.7(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1c

Cr−C(1)	1.834(4)	Cr−C(9)	2.201(3)
Cr−C(2)	1.846(4)	C(4)−C(10)	1.441(5)
Cr−C(3)	1.840(4)	C(1)−C(2)	1.189(5)
Cr−C(4)	2.217(3)	O(1)−C(1)	1.167(4)
Cr−C(5)	2.203(3)	O(2)−C(2)	1.157(4)
Cr−C(6)	2.210(3)	O(3)−C(3)	1.150(4)
Cr−C(7)	2.209(4)	C(11)−C(12)	1.484(5)
Cr−C(8)	2.212(3)	C(12)−N(1)	1.464(4)
O(1)−C(1)−Cr	179.1(3)	C(2)−Cr−C(3)	89.6(2)
O(2)−C(2)−Cr	177.9(3)	C(3)−Cr−C(1)	88.4(2)
O(3)−C(3)−Cr	179.2(3)	C(10)−C(11)−C(12)	175.6(4)
C(1)−Cr−C(2)	88.3(2)	C(4)−C(10)−C(11)	179.0(4)

To obtain more details related to the cyclopalladated complexes using NMR spectroscopy, we performed the reaction of equimolar amounts of **2a**,**b** with pyridine (CH_2Cl_2, 25 °C, Scheme 2), affording a monomeric species {Pd-*trans*-C[(Ph)Cr(CO)$_3$]=C(Cl)CHRNMe$_2$(Cl)-(Py)} (**3a**, R = H; **3b**, R = Me) as a yellow solid in almost quantitative yield. Compounds **3a**,**b** are air-stable and show high solubility in medium polar solvents. In the ^{1}H NMR spectra of **3a**,**b** the aromatic protons are shifted upfield relative to the arene resonances of the compounds **1a**,**b** and appear in the region between 5.15 and 4.70 ppm. The coordination of nitrogen to the palladium is reflected by the low field of the ^{1}H NMR signals of the NMe$_2$, CH, and CH$_2$ groups. Furthermore, in the $^{13}C\{^1H\}$ NMR spectrum of **3a**,**b** the chlorovinyl palladium group provides two distinct resonances for the carbon−carbon double bond, i.e., a characteristic downfield signal (δ 140.8 and 139.7 ppm, respectively) of an sp^2 carbon bound to a chlorine atom and an upfield signal (δ 125.5 and 124.9 ppm, respectively) for the carbon bound to the palladium center. The observed *trans* stereochemistry of the chloro atom attached to vinyl group with respect to palladium center is the same as observed for other chloropalladation reactions of heterosubstituted alkynes.[6d]

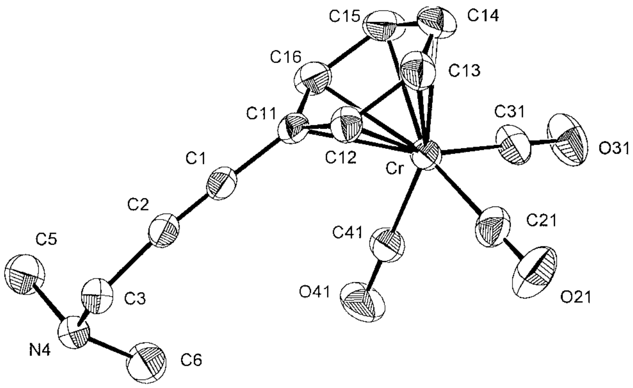


Figure 1. Molecular structure of Me$_2$NCH$_2$C≡CPh[Cr(CO)$_3$] (**1a**, H atoms omitted) with thermal ellipsoids at the 30% probability level.

It is noteworthy to mention that the reaction of **1c** with Li$_2$PdCl$_4$ afforded only decomposition products and unreacted starting compound **1c** even using different conditions (higher temperatures and reaction time), indicating that the presence of a more sterically demanding group bound to the nitrogen atom plays an important role in the C≡C bond reactivity toward the chloropalladation reaction. Furthermore, we have recently demonstrated that the presence of bulky groups

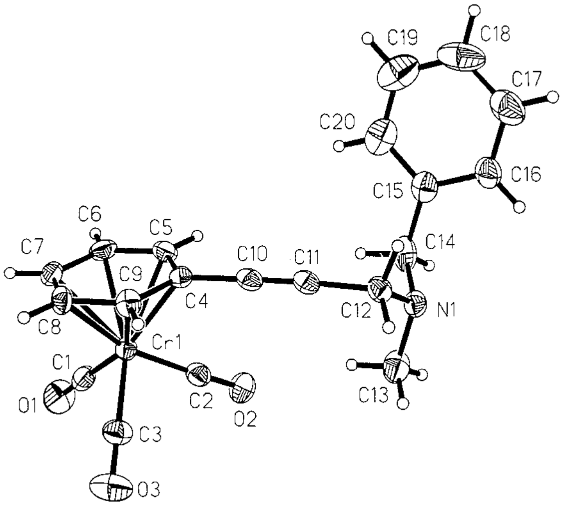
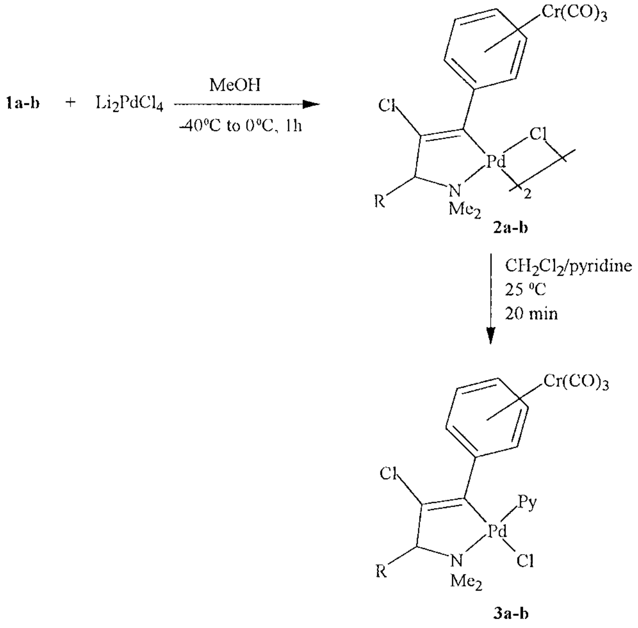


Figure 2. Molecular structure of $(PhCH_2)(Me)NCH_2C{\equiv}CPh[Cr(CO)_3]$ (**1c**) with thermal ellipsoids at the 50% probability level.

Scheme 2



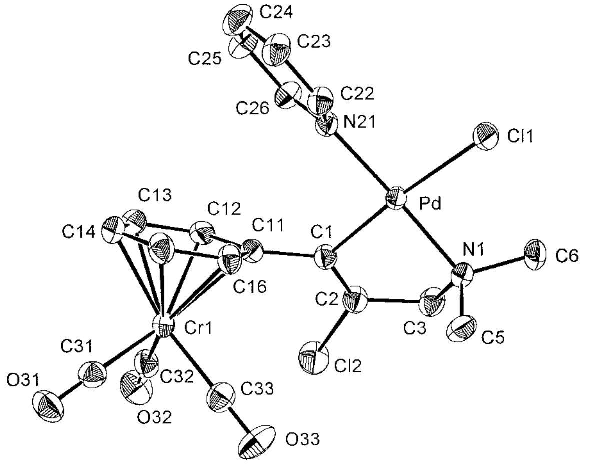


Figure 3. Molecular structure of $\{Pd$-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(Cl)(py)\}$ (**3a**, H atoms omitted) with thermal ellipsoids at the 30% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3a

Cr−C(31)	1.834(5)	Cr−C(32)	1.863(5)
Cr−C(33)	1.843(5)	Cr−C(13)	2.205(4)
Cr−C(12)	2.206(4)	Cr−C(16)	2.213(4)
Cr−C(15)	2.214(5)	Cr−C(14)	2.214(5)
Cr−C(11)	2.249(4)	Pd−C(1)	2.010(4)
Pd−N(21)	2.049(3)	Pd−N(4)	2.076(3)
Pd−Cl(1)	2.3875(12)		
Cr−C(31)−O(31)	179.4(4)	Cr−C(32)−O(32)	179.2(4)
Cr−C(33)−O(33)	179.5(4)	N(21)−Pd−N(4)	175.14(13)
C(1)−Pd−Cl(1)	175.35(11)	C(1)−Pd−N(4)	82.15(14)
N(21)−Pd−Cl(1)	90.36(9)	Cl(1)−Pd−N(4)	93.81(10)

attached to the C≡C bond also controls the activation of the triple bond.[6b] Thus the activation of the triple bond toward the chloropalladation reaction seems to be dependent on the presence of the sterically demanding groups either attached directly to the C≡C bond and/or bound to a heteroatom unit.

Molecular Structure of $\{Pd$-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(Cl)(Py)\}$ (3a). Crystal data for **3a** are summarized in Table 1, refinement details are discussed in the Experimental Section, and selected bond distances and angles are listed in Table 4. Molecular geometry and atom-labeling scheme are shown in Figure 3. Compound **3a** crystallizes in the triclinic system, and the lattice fits the $P\bar{1}$ symmetry group. The molecule is constituted by two subunits determined by Cr and Pd atoms which contain a five-membered metallacycle formed by the palladium, the nitrogen, and methylene group and carbon atoms involved in the double bond, thus confirming that chloropalladation had taken place on the propargyl unit. The metallacycle and the arene moieties are not coplanar. The metallacycle unit is twisted around the C(11)−C(1) axis presumably as a consequence of steric effects arising from the pyridine and arene ligands. The geometry at palladium is that of a slightly distorted square plane with angles at Pd in the ranges 82.15(14)−93.81(10)° and 175.14(13)−175.35(11)°. The Pd−C(1), Pd−N(21), Pd−Cl(1), and Pd−N(4) bond distances [2.010(4), 2.049(3), 2.3875(12), and 2.076(3) Å, respectively] are similar to the related cyclopalladated analogue.[9] The $Cr(CO)_3$ adopts a nearly staggered conformation with similar $Cr{-}C_{arene}$ and Cr−CO bond distances that compare well with those found for **1a** and **1c**.

Conclusions

This work establishes that chromium−arene compounds containing propargylamines can be easily prepared in good yields from the C−C coupling reaction between (η^6-chlorobenzene)tricarbonylchromium and propargylamines assisted by palladium/copper catalysts. These chromium−arene complexes incorporating propargylamines undergo a chloropalladation reaction, affording heterobimetallic cyclopalladated compounds that are not accessible by classical cyclopalladation methods. The activation of the triple bond toward the chloropalladation reaction seems to be dependent on the presence of the sterically demanding groups either

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(9) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451.

attached directly to C≡C bond and/or bound to the heteroatom unit. Moreover, since the chloropalladation reaction can be performed with a large variety of nitrogen- and sulfur-containing alkynes, and with group 10 metals,[6] this method opens the possibility for the synthesis of a large family of heterobimetallic cyclometalated (η^6-arene)tricarbonylchromium, and research toward this goal is currently under investigation in our laboratory.

Experimental Section

General Procedures. All manipulations were performed using vacuum-line or Schlenk techniques under a purified atmosphere. Solvents were stored under argon or vacuum prior to use. Chlorobenzene, hexane, THF, and Et_2O were distilled from Na/benzophenone ketyl, and CH_2Cl_2 was distilled from P_2O_5. 1-Dimethylamino-2-propyne (Aldrich) was purchased and used as received. (η^6-chlorobenzene)tricarbonylchromium was prepared following literature procedures.[10] Lithium tetrachloropalladate was prepared by the reaction of an excess amount (20 mol %) of lithium chloride with palladium chloride in methanol at reflux temperature. NMR spectra were recorded on a Varian-300 spectrometer in Teflon-valved NMR tubes at ambient probe temperature. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H and $^{13}C\{^1H\}$ solvent peaks. Coupling constants are reported in hertz. Mass spectra were obtained using the direct insertion probe method on a VG Analytical Trio I instrument operating at 70 eV. Elemental analyses were performed by the Central Analítica IQ/UFRGS (Porto Alegre, Brazil).

General Procedure for the Preparation of Arene−Chromium Complexes Containing N-Functionalized Alkynes. (η^6-C_6H_5Cl)$Cr(CO)_3$ (2.98 g, 12.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.42 g, 0.60 mmol), and CuI (0.11 g, 0.60 mmol) were dissolved in THF (90 mL) and NEt_3 (45 mL), and a solution of the alkyne (18.2 mmol) in THF (10 mL) was added dropwise over a period of 50 min at 25 °C. The resulting mixture was refluxed for 12 h. After cooling to room temperature diethyl ether (50 mL) was added, the suspension was filtered, and the solvent was removed from the filtrate, yielding a black residue. The residue was chromatographed on silica gel using ethyl acetate as eluent and the intense yellow band was collected.

$Me_2NCH_2C{\equiv}CPh[Cr(CO)_3]$ (1a). 1a was obtained as a bright yellow solid (2.48 g, 70%). ^1H NMR ($CDCl_3$): δ 5.47 (d, 2H, $^3J_{HH} = 6.2$, *H^2 and H^6*, Ph), 5.34 (t, 1H, $^3J_{HH} = 5.7$, H^4, Ph), 5.27 (d, 2H, $^3J_{HH} = 5.7$, *H^3 and H^5*, Ph), 3.44 (s, 2H, CH_2-NMe_2), 2.36 (s, 6H, CH_2NMe_2). $^{13}C\{^1H\}$ ($CDCl_3$): δ 232.1 (C≡O), 94.9, 91.7, 90.6 (aromatic), 90.5 (C_{ipso}), 85.4, 81.3 (C≡C), 48.2 (CH_2NMe_2), 44.1 (CH_2NMe_2). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$: 2233 (w); ν_{CO}: 1973 (s), 1905 (m), 1866 (m). Anal. Calcd for $C_{14}H_{13}CrNO_3$: C, 56.94; H, 4.40; N, 4.74. Found: C, 56.80; H, 4.38; N, 4.70. MS (EI, *m/z*): 295 $[M]^+$, 239 $[M - 2\ CO]^+$, 211 $[M - 3\ CO]^+$.

$Me_2NC(H)(Me)C{\equiv}CPh[Cr(CO)_3]$ (1b). 1b was obtained as a gold-yellow solid (2.78 g, 75%). ^1H NMR ($CDCl_3$): δ 5.44 (d, 2H, $^3J_{HH} = 6.2$, *H^2 and H^6*, Ph), 5.34 (t, 1H, $^3J_{HH} = 5.7$, H^4, Ph), 5.20 (d, 2H, $^3J_{HH} = 5.7$, *H^3 and H^5*, Ph), 3.67 (q, 1H, $^3J_{HH} = 6.6$, CHMe), 2.30 (s, 6H, NMe_2), 1.40 (d, 3H, $^3J_{HH} = 6.6$, CHMe). $^{13}C\{^1H\}$($CDCl_3$): δ 232.1 (C≡O), 94.7, 91.9, 90.9, 90.2 (aromatic) 88.7, 81.5 (C≡C), 52.6 (CHMe), 41.3 (NMe_2), 19.7 (CHMe). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$: 2227 (w); ν_{CO} 1954 (s), 1891 (s). Anal. Calcd for $C_{15}H_{15}CrNO_3$: C, 58.25; H, 4.85; N, 4.53. Found: C, 58.12; H, 4.76; N, 4.43. MS (EI, *m/z*): 309 $[M]^+$, 253 $[M - 2\ CO]^+$, 225 $[M - 3\ CO]^+$.

$(PhCH_2)(Me)NCH_2C{\equiv}CPh[Cr(CO)_3]$ (1c). 1c was obtained as a gold-yellow solid (2.61 g, 71%). ^1H NMR ($CDCl_3$): δ 7.34 (m, 5H, aromatic) 5.46 (d, 2H, $^3J_{HH} = 6.2$, *H^2 and H^6*, Ph), 5.34 (t, 1H, $^3J_{HH} = 5.7$, H^4, Ph), 5.25 (d, 2H, $^3J_{HH} = 5.7$, *H^3 and H^5*, Ph), 3.62 (s, 2H, CH_2N), 3.48 (s, 2H, CH_2Ph), 2.40 (s, 3H, NMe). $^{13}C\{^1H\}$($CDCl_3$): δ 232.1 (C≡O), 138.1, 129. 2, 128.3, 127.3 (CH_2Ph), 95.0, 91.7, 91.0, 90.6 (aromatic) 85.4, 81.7 (C≡C), 60.1 (CH_2Ph), 45.4 (CH_2N), 41.9 (NMe). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$: 2227 (w); ν_{CO} 1964 (s), 1891 (s). Anal. Calcd for $C_{20}H_{17}CrNO_3$: C, 64.69; H, 4.58; N, 3.77. Found: C, 64.56; H, 4.53; N, 3.68. MS (EI, *m/z*): 371 $[M]^+$, 287 $[M - 3\ CO]^+$.

{Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(\mu\text{-}Cl)\}_2$ (2a). A solution of lithium tetrachloropalladate (0.78 g, 3.00 mmol) was cooled to −40 °C, and a solution of **1a** (0.88 g, 3.00 mmol) in MeOH (80 mL) was added dropwise within 15 min. The reaction mixture was warmed to 0 °C and stirred for 1 h, affording a yellow-brown suspension. The solution was filtered, and the solid was washed with hexane (3 × 10 mL) to afford a yellow powder that was dried under vacuum (0.62 g, 64%). IR (KBr, cm^{-1}): ν_{CO} 1961 (s), 1875 (s). Anal. Calcd for $C_{28}H_{26}Cl_4Cr_2N_2O_6Pd_2$: C, 35.56; H, 2.75; N, 2.96. Found: C, 35.47; H, 2.71; N, 2.93.

{Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH(Me)NMe_2(\mu\text{-}Cl)\}_2$ (2b). This compound was prepared by the procedure outlined for **2a**, using 0.40 g of Li_2PdCl_4 (1.54 mmol) and 0.47 g of **1b** (1.54 mmol). The complex was isolated as yellow powder (0.50 g, 67%). IR (KBr, cm^{-1}): ν_{CO} 1957 (s), 1868 (s). Anal. Calcd for $C_{30}H_{30}Cl_4Cr_2N_2O_6Pd_2$: C, 37.00; H, 3.08; N, 2.88. Found: C, 36.65; H, 2.87; N, 2.71.

{Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2NMe_2(Cl)(Py)\}$ (3a). A CH_2Cl_2 solution (10 mL) of pyridine (0.08 g, 1.00 mmol) was added dropwise (5 min) to a CH_2Cl_2 suspension (30 mL) of **2a** (0.40 g, 0.42 mmol) at 25 °C. The mixture was stirred for 20 min, affording a cloudy orange solution, which after filtration in Celite yielded an orange filtrate. The volatiles were removed under vacuum to afford an orange solid. Recrystallization from CH_2Cl_2/hexane yielded a yellow solid (0.44 g, 95%). ^1H NMR ($CDCl_3$): δ 8.52 (d, 2H, $^3J_{HH} = 5.2$, *H^2 and H^6*, Py), 7.60 (t, 1H, $^3J_{HH} = 5.2$, H^4, Py), 7.19 (m, 2H, *H^3 and H^5*, Py), 5.15 (d, 2H, $^3J_{HH} = 5.7$, *H^2 and H^6*, Ph), 4.96 (d, 1H, $^3J_{HH} = 5.7$, H^4, Ph), 4.84 (t, 2H, $^3J_{HH} = 5.7$, *H^3 and H^5*, Ph), 3.71 (s, 2H, CH_2-NMe_2), 2.92 (s, 6H, CH_2NMe_2). $^{13}C\{^1H\}$($CDCl_3$): δ 233.7 (C≡O), 140.8 (=C(Cl)) 153.8, 138.3, 125.4 (aromatic, CH, py), 125.5 (Pd−C=), 110.1 (C_{ipso}), 95.3, 91.5, 90.0 (aromatic, CH, Ph), 76.9 (CH_2N), 53.3 ($N(CH_3)_2$). IR (KBr, cm^{-1}): ν_{CO} 1968 (s), 1898 (s). Anal. Calcd for $C_{19}H_{18}Cl_2CrN_2O_3Pd$: C, 41.34; H, 3.26; N, 5.08. Found: C, 41.23; H, 3.20; N, 5.02.

{Pd-*trans*-$C[(Ph)Cr(CO)_3]{=}C(Cl)CH(Me)NMe_2(Cl)(Py)\}$ (3b). This compound was prepared by the procedure outlined for **3a**, using 0.08 g of pyridine (1.00 mmol) and 0.41 g of **2b** (0.42 mmol). The complex was isolated as an yellow-orange powder (0.44 g, 92%). ^1H NMR ($CDCl_3$): δ 8.56 (d, 2H, $^3J_{HH} = 5.2$, *$H^2$and H^6*, Py), 7.62 (t, 1H, $^3J_{HH} = 5.2$, H^4, Py), 7.11 (m, 2H, *H^3 and H^5*, Py), 5.31 (d, 1H, $^3J_{HH} = 5.8$, H^2, Ph), 5.17 (d, 1H, $^3J_{HH} = 6.8$, H^6, Ph), 5.00 (m, 2H, *H^3 and H^5*, Ph), 4.70 (t, 1H, $^3J_{HH} = 5.8$, H^4, Ph), 3.32 (q, 1H, $^3J_{HH} = 6.3$, CHMe), 3.11 (s, 3H, NMe_2), 2.69 (s, 3H, NMe_2), 1.77 (d, 3H, $^3J_{HH} = 6.3$, CHMe). $^{13}C\{^1H\}$($CDCl_3$): δ 233.2 (C≡O), 139.7 (=C(Cl)), 153.4, 137.7, 128.1 (aromatic, CH, py), 124.9 (Pd−C=), 109.8 (C_{ipso}), 95.3, 94.2, 90.9, 90.0, 89.3 (aromatic, CH, Ph), 53.2 (CHMe), 48.9 (NMe_2), 20.0 (CHMe). IR (KBr, cm^{-1}): ν_{CO} 1954 (s), 1892 (s). Anal. Calcd for $C_{20}H_{20}Cl_2CrN_2O_3Pd$: C, 42.44; H, 3.53; N, 4.95. Found: C, 42.07; H, 3.51; N, 4.88.

X-ray Crystallography. The structures of **1a** and **3a** were determined at the Universidade Federal de Santa Maria, Brazil, by M. Hörner. The structure of **1c** was determined at the University of Minnesota by V. G. Young, Jr. Crystal data, data collection details, and solution and refinement procedures are collected in Table 1. Additional comments specific to each structure follow.

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(10) Mahaffy, C. A. L.; Pauson, P. *Inorg. Synth.* **1990**, *28*, 137.

$Me_2NCH_2C{\equiv}CPh[Cr(CO)_3]$ (1a). Crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution containing **1a** at room temperature. All non-H atoms were refined with anisotropic displacement parameters, and H atoms were refined with isotropic thermal parameters.

$(CH_2Ph)(Me)NCH_2C{\equiv}CPh[Cr(CO)_3]$ (1c). Crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution containing **1c** at room temperature. All non-H atoms were refined with anisotropic displacement parameters, and all H atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

$\{\underline{Pd\text{-}\textit{trans}\text{-}C[(Ph)Cr(CO)_3]{=}C(Cl)CH_2N}Me_2(Cl)(Py)\}$ (3a). Crystals were obtained by recrystallization from $CHCl_3$ at −30 °C. The complex crystallizes together with a chloroform molecule which is disordered in the unit cell. All non-H atoms were refined with anisotropic displacement parameters, with the exception of the chlorine atoms from $CHCl_3$, which are disordered over two sites, each one with 50% occupancy, and refined isotropically. All H atoms were placed in ideal positions and refined as riding atoms with group isotropic displacement parameters.

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Supporting Information Available: Tables of complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1a**, **1c**, and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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