The mean Ta–Cl bond distance for Cl1, Cl2, and Cl4 is as expected 2.446 Å but a shorter bond length of 2.295 Å is observed for Ta–Cl3 which is an eclipsed conformation with one of the C–Me bonds of the ring (see Figure 2), giving bigger angles with the nearest Cl atoms.

The tantalum–C(ylide) bond length of 2.349 (29) Å corresponds to a single bond and is of the same order than that found for a μ-$CHPMe_3$ bridging group.[2b] The Ta–C11–P angle of 125 (1)° and the four equivalent P–C bond lengths averaging 1.841 Å are in the range of those observed for other metal–neutral phosphorus ylide complexes reported.[7]

The reactions of these compounds with an excess of the methylenephosphoranes in order to obtain bidentate anionic ylide $(CH_2)_2PR_2$ or alternatively anionic ylide $Ta{=}CHPR_3$ complexes are being studied.

Acknowledgment. We gratefully acknowledge financial support from Comisión Asesora de Investigación Científica y Técnica (Ref 2001-83). This communication is dedicated to Professor R. Usón on the occasion of his 60th birthday.

Registry No. **1**, 108418-44-6; **2**, 108418-45-7; **3**, 108418-46-8; **4**, 108418-47-9; $(\eta^5$–$C_5Me_5)TaCl_4$, 71414-47-6; $CH_2{=}PMe_3$, 14580-91-7; $CH_2{=}PPhMe_2$, 29949-96-0; $CH_2{=}PMePh_2$, 4554-22-7; $CH_2{=}PPh_3$, 3487-44-3.

Supplementary Material Available: ORTEP drawings and tables of crystal data, fractional coordinates and thermal parameters, least-squares planes, torsion angles, and bond lengths and angles (41 pages); a listing structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

X-ray Crystal Structure of the Triple-Decker-Sandwich Complex Bis(η^6-mesitylene)(μ-η^6:η^6-mesitylene)dichromium

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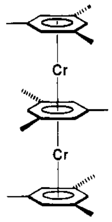
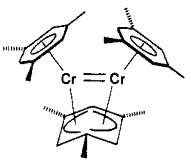
Summary: The X-ray crystal structure of the previously reported tris(mesitylene)dichromium triple-decker-sandwich complex, prepared by co-condensation of Cr vapor with mesitylene at high metal loadings, is described. The material is disordered in the solid with all possible ring methyl positions being half occupied. The three aromatic rings are parallel and nearly perfectly eclipsed when viewed down the threefold Cr/Cr axis which lies normal to the ring planes.

Recently we reported that the reaction of chromium vapor with mesitylene at high metal-to-ligand ratios leads to the formation of an unusual dinuclear complex with the stoichiometry tris(mesitylene)dichromium. On the basis of evidence from variable-temperature ^1H and ^{13}C NMR spectroscopy, the dichromium species was formulated as the novel triple-decker-sandwich structure 1,[1] the first homoleptic triple-decker containing bridging and terminal arene ligands.

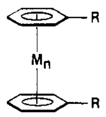
As previously noted,[1] the NMR data in this instance are not sufficient for a completely unambiguous structural assignment. That is, they do not strictly rule out alternative structures of equivalent stoichiometry but lower symmetry than 1, provided that these alternative structures are rapidly fluxional below −90 °C on the NMR time scale. One such hypothetical structure, for which there exists some literature precedent,[2] is 2. In our previous account we disfavored such structures on the basis that they do not as readily explain the matrix-isolation evidence of Lamanna[1] and Ozin[3] for the stepwise formation of higher arene–metal species with more than two metal atoms. However, it was apparent from the outset that a conclusive resolution of this issue would only be provided by an X-ray crystal structure.



1



2



3

Preliminary attempts to obtain X-ray quality crystals of tris(mesitylene)dichromium were hampered by its tendency to crystallize in the form of thin sheets and by its extreme oxygen sensitivity. These problems were overcome by conducting crystallizations in a N_2-filled drybox at −40 °C by allowing petroleum ether vapor to diffuse into a concentrated solution of 1 in diethyl ether. The resultant deep purple crystals were loaded into glass capillaries and sealed under N_2. Crystal data: $C_{27}H_{36}Cr_2$, fw 464.58, rhombohedral, space group $R\bar{3}m$, a = 11.063 (3) Å, α = 43.97 (2)°, Z = 1, ω–2θ scans, 497 data of which 409 with $I > 1\sigma(\mathbf{I})$ were used, R = 0.029, R_W = 0.039. Additional details of the crystal structure determination are given in the supplementary material.

The structural features in 1 generally resemble those reported for the closely related bis(η^5-cyclopentadienyl)(μ-η^6:η^6-arene)divanadium[4] and bis(η^5-cyclo-

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[1] (1) Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096.

[2] (2) (a) Jonas, K.; Wiskamp, V.; Tsay, Y.H.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480. (b) Müller, J.; Holzinger, W.; Köhler, F. H. *Chem. Ber.* **1976**, *109*, 1222. (c) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1976**, *15*, 2511. (d) Elschenbroich, C.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905.

[3] (3) (a) Ozin, G. A.; Francis, C. G.; Andrews, M. *Inorg. Synth.* **1983**, *22*, 116. (b) Ozin, G. A.; Huber, H.; Francis, C. G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 402; *Angew. Chem.* **1980**, *92*, 409. (c) Ozin, G. A.; Huber, H.; Francis, C. G. *Inorg. Chem.* **1980**, *19*, 219. (d) Ozin, G. A.; Francis, C. G.; Huber, H.X.; Andrews, M.; Nazar, L. *J. Am. Chem. Soc.* **1981**, *103*, 2453. (e) Ozin, G. A.; Huber, H.; Francis, C. G. *J. Am. Chem. Soc.* **1979**, *101*, 6250. (f) Ozin, G. A.; Andrews, M. P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 212; *Angew. Chem. Suppl.* **1982**, 381; *Angew. Chem.* **1982**, *94*, 219. (g) Ozin, G. A. *Chemtech* **1985**, *15*, 488. (h) Ozin, G. A.; Andrews, M. P.; West, R. *Inorg. Chem.* **1986**, *25*, 580. (i) Ozin, G. A.; Andrews, M. P. *J. Phys. Chem.* **1986**, *90*, 1245. (j) Ozin, G. A.; Andrews, M. P. *J. Phys. Chem.* **1986**, *90*, 2938. (k) Ozin, G. A.; Andrews, M. P. *J. Phys. Chem.* **1986**, *90*, 3140. (l) Ozin, G. A.; Andrews, M. P. *Inorg. Chem.* **1986**, *25*, 2587. (m) Ozin, G. A.; Andrews, M. P. *J. Phys. Chem.* **1986**, *90*, 3353.

[4] (4) Jonas, K.; Duff, A. W.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.

0276-7333/87/2306-1583$01.50/0

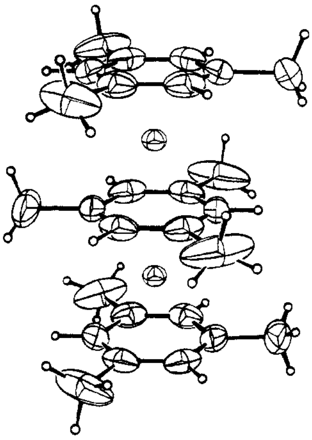

Figure 1. ORTEP drawing (50% probability ellipsoids) of tris(mesitylene)dichromium. C1 and C3 are the ring atoms, and C2 and C4 are the methyl C atoms in the central ring and terminal ring, respectively. The rings are as shown in the figure. The methyl groups on each ring could occupy either of two alternative sets of ring positions. For each ring the orientation has been chosen arbitrarily: the actual orientation of the methyl rings cannot be determined from the X-ray data. (See supplementary material for a discussion of the disorder.)

Table I. Selected Bond Distances (Å) and Angles (deg) for $(\eta^6\text{-}C_6Me_3H_3)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6Me_3H_3)Cr_2$ (1)[a,b]

Bond Distances			
Cr–C1	2.190 (3)	C3–C3′	1.402 (2)
Cr–C3	2.131 (1)	C3–C3″	1.413 (2)
C1–C1′	1.417 (4)	C3–C4	1.517 (4)
C1–C2	1.510 (10)	Cr–Cr	3.338 (1)
Bond Angles			
C1′–C1–C1′	120	C3′–C3–C4	116.9 (4)
C1′–C1–C2	120	C3″–C3–C4	123.1 (4)
C3′–C3–C3″	120		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Since the central ring has $\bar{3}m$ crystallographic symmetry, there is only one C–C ring distance and all of the C–C–C angles are 120°, whereas the terminal rings have $3m$ crystallographic symmetry so that there are two alternating independent C–C bond distances in the ring, and the two external C–C–C angles are not equal, even though all Cr–C distances are the same.

pentadienyl)(μ-η^5:η^5-cyclopentadienyl)dinickel(1+)[5] triple-decker-sandwich compounds. As shown in Figure 1, all three mesitylene rings are planar, parallel, and nearly perfectly eclipsed when viewed down the threefold Cr–Cr axis which lies normal to the aromatic ring planes. Pertinent bond lengths and angles are given in Table I. The relative positions of methyl groups on adjacent rings cannot be determined due to the crystallographic disorder. (See supplementary material for further discussion.) The distance from Cr to the central ring plane is 1.669 (1) Å and to the terminal ring plane is 1.600 (1) Å. This should be compared with the Cr to ring distance of 1.609 (1) Å found in bis(benzene)chromium.[6] The elongated Cr bond to the bridging mesitylene ring in 1 accords well with the apparent susceptibility of this bond to thermolytic and oxidative cleavage.[1]

The Cr–Cr distance of 3.338 (1) Å in 1 is considerably longer than the average intermetallic spacing of 2.221 Å in the isoelectronic and structurally related tricarbonyl-bridged complex bis(η^6-benzene)tris(μ-carbonyl)dichromium[7] possessing a formal metal–metal triple bond. The sum of the estimated single-bond covalent radii of Cr(0) is 2.96 Å,[8] suggesting that little or no direct interaction exists between the Cr centers in 1.[9] However, it is important to note that an elongated Cr–Cr bond of 3.281 (1) Å has been previously reported for the dimeric complex $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]_2$.[8a]

The crystal structure confirms our earlier spectroscopic interpretations[1] and provides further support for the probable existence of higher nuclearity $(\text{arene})_nM_{n-1}$ multiple-decker-sandwich oligomers and polymers.[10] We contend that such extended chain complexes most readily account for the stepwise formation of polynuclear arene–metal species in matrix-scale reactions of Cr, Mo, V, and Ti with arene substrates.[1,3] This is contrary to structural formulations originally proposed by Ozin and co-workers in which "arene- or polymer-stabilized metal clusters" consisting of two or more bound metal atoms sandwiched between a single pair of arene rings as in 3 ($n \geq 2$) were suggested.[3]

Acknowledgment. W.M.L. wishes to thank Prof. Walter Siebert (University of Heidelberg) and Prof. Jeremy Burdett (University of Chicago) for helpful discussions.

Supplementary Material Available: Further crystallographic details and a discussion of the disorder possibilities and their resolution, tables of atomic coordinates, anisotropic displacement parameters, and hydrogen coordinates, and stereo ORTEP and packing diagrams (9 pages); a listing of structure factors (3 pages). Ordering information is given on any current masthead page.

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[5] Dubler, E.; Textor, M.; Oswald, H.-R.; Salzer, A. *Angew. Chem.*, **1974**, *86*, 125; *Agnew. Chem., Int. Ed. Engl.* **1974**, *13*, 135.

[6] Keulen, E.; Jellinek, F. *J. Organomet. Chem.* **1966**, *5*, 490.

[7] Knoll, L.; Reiss, K.; Schafer, J.; Klufers, P. *J. Organomet. Chem.* **1980**, *193*, C40.

[8] (a) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749. (b) Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1966**, *5*, 1851.

[9] Metal–metal bonding through the center of the bridging ring in triple-decker-sandwich complexes has been suggested in at least one instance based on the comparatively short Mo–Mo distance (2.647 Å) and the 28-electron configuration in the complex $(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)Mo_2$ (cf. Scherer, O. J.; Sitzmann, H.; Wolmerhauser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351).

[10] Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805.

Formation of $[\overline{Ru\{HN{=}C(Ph)OC}{=}CHPh\}(CO)Cl\{P(4\text{-}MeC_6H_4)_3\}_2]$. An Anomalous Insertion Reaction of Phenylacetylene with $[Ru(CO)ClH(3,5\text{-}Me_2Hpz)\{P(4\text{-}MeC_6H_4)_3\}_2]$ in Ethanol/Dichloromethane

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Summary: An unusual reaction of $[Ru(CO)ClH(3,5\text{-}Me_2Hpz)\{P(p\text{-}MeC_6H_4)_3\}_2]$ with phenylacetylene in EtOH or $EtOH/CH_2Cl_2$ is described, in which a complex containing a new five-membered ruthenacycle, $[\overline{Ru\{NH{=}C(Ph)OC}{=}CHPh\}(CO)Cl\{P(p\text{-}MeC_6H_4)_3\}_2]$, is formed, whose structure has been determined by X-ray crystallography. The reaction in CH_2Cl_2 yields the expected complex $[Ru(CO)Cl(HC{=}CHPh)(3,5\text{-}Me_2Hpz)\{P(p\text{-}MeC_6H_4)_3\}_2]$, resulting from insertion of phenylacetylene into the Ru–H bond.