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LIGAND WRAPPING AROUND CHROMIUM: REACTIONS OF DIPHENYLMETHANE, 1,4-DIPHENYLBUTANE, BENZYL ETHER, AND BENZYL SULFIDE WITH CHROMIUM ATOMS

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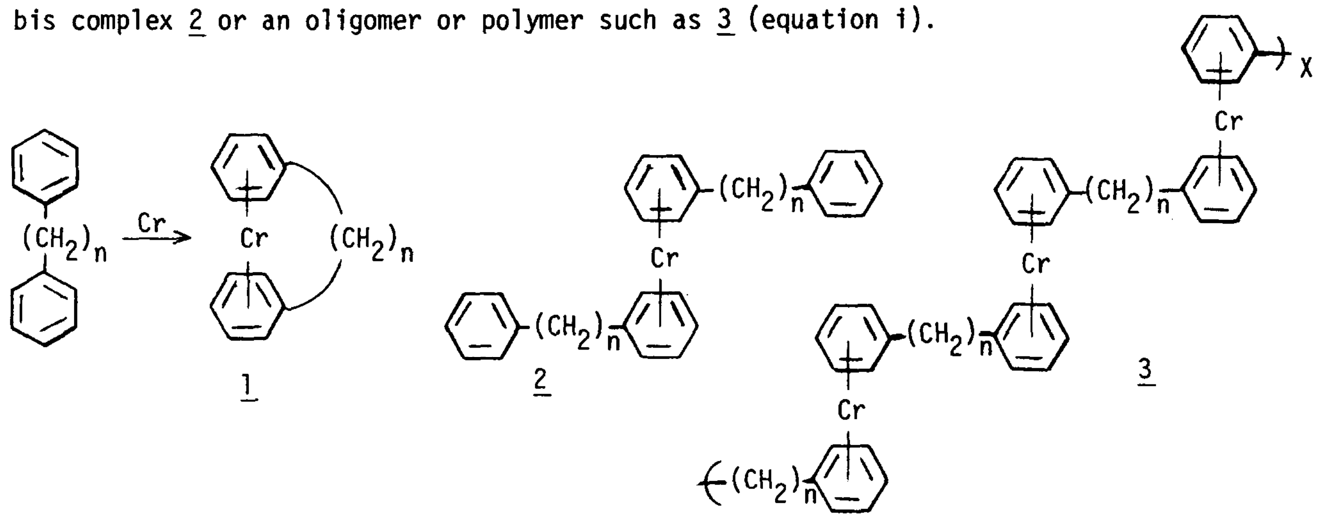
The cocondensation of chromium atoms with benzenoid compounds has provided a useful entry into a variety of otherwise difficultly accessible bis(arene)chromium complexes.[1-4] However, the use of polyphenylated organic precursors, which may give rise to a variety of novel complex types, remains relatively unexplored. For instance, the cocondensation of α,ω-diphenylalkanes with chromium atoms could in theory give rise to three types of products: the monomeric "wrapped" species 1, the bis complex 2 or an oligomer or polymer such as 3 (equation i).

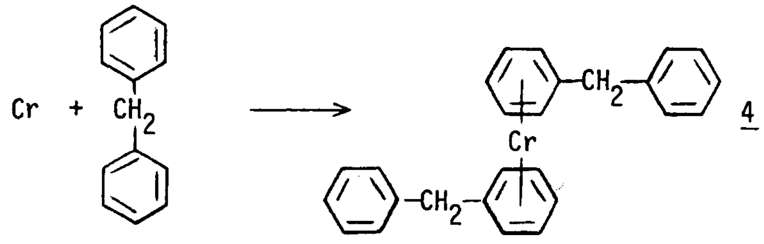
(i)



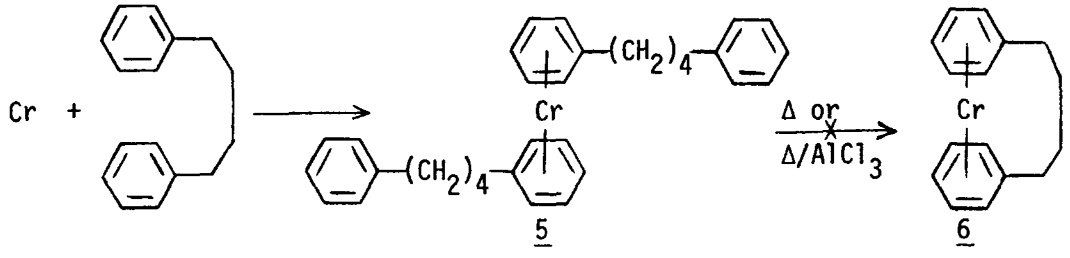
1 2 3

In this communication, we report the following observations pertaining to the "wrapping" of diphenylated ligands around chromium: (a) cocondensation of chromium atoms with neat diphenylmethane, 1,4-diphenylbutane, and benzyl ether affords complexes of the type 2 as the only detectable products; (b) cocondensation of chromium atoms with benzyl sulfide results mainly in desulfurization; (c) thermal and chemical attempts to effect conversions such as 2 → 1 result instead in total ligand release; and (d) cocondensation of chromium atoms with 1,4-diphenylbutane diluted in hexadecane affords some complex of the type 1.

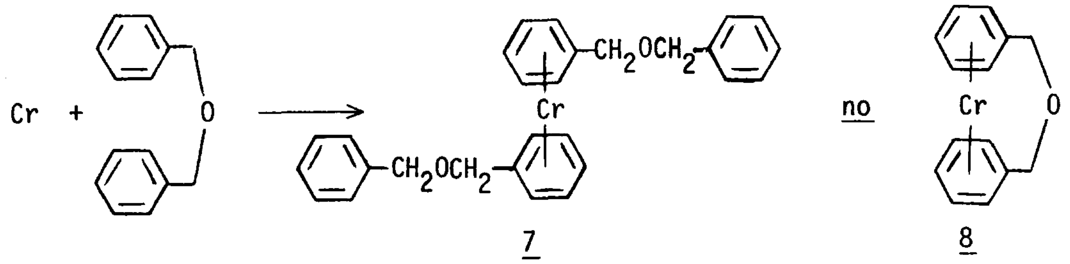
(ii)



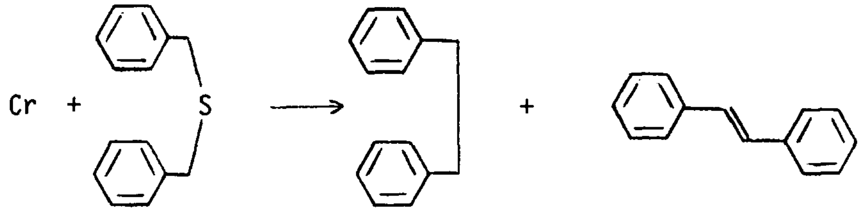
(iii)



(iv)



(v)



Diphenylmethane (60 mmol) and chromium atoms (2.9 mmol)[5] were cocondensed at 77°K and $\leq 10^{-4}$ torr in the type of metal atom reactor employed by Skell and Klabunde.[6-8] Afterwards, the cooling bath was removed and the matrix allowed to warm to room temperature over a one hour period under static vacuum. Excess diphenylmethane was then pumped into a cold trap and the yellow reactor residue extracted with ether. The ^{13}C nmr of the extract showed only a single product which contained both complexed (C_6D_6; 93.0, 78.0, 75.5 ppm)[4] and uncomplexed (142.6, 128.7, 128.6, 126.2) arene carbons and an aliphatic carbon (41.8). This is consistent only with the indicated structural assignment 4 (equation ii) and shows that no soluble product of the type 1 or 3 was formed. Purification was achieved by sublimation (90-110°, 10^{-5} torr), which yielded a yellow-green solid, mp 132-135°C (252 mg, 0.650 mmol, 22% yield based upon chromium). Mass spectrum: m/e 388 (8%) 220 (8), 168 (100). Even after repeated sublimations, paramagnetic impurities remained which precluded obtaining a ^1H nmr spectrum. In other experiments, up to a 71% yield of 4 was obtained.

Chromium atoms (2.5 mmol)[5] and 1,4-diphenylbutane (46 mmol) were cocondensed under similar conditions (equation iii). Only a single product was present in the unpurified reactor extract, as indicated by ^{13}C nmr. Its spectrum (C_6D_6; 142.7, 128.7, 128.6, 126.0, 97.1, 77.3, 75.3, 36.2, 35.9, 32.6, 31.5 ppm) is consistent only with the structural assignment 5.[9] Sublimation (150°, 10^{-5} torr) afforded 241 mg (0.511 mmol) of a dark green solid, mp 56-57°C. Mass spectrum: m/e 472 (2%), 264 (58), 210 (41), 90 (64), 89 (100). ^1H nmr (δ, C_6D_6): multiplets centered at 1.55 (8H) and 2.43 (8H), broad absorbance at 4.20 (10H, complexed rings),[9] 7.13 ppm (10H, uncomplexed rings). When other investigators attempted the synthesis of 5 utilizing conventional reducing Freidel-Crafts conditions ($CrCl_3$, $AlCl_3$), only tetralin complexes were obtained, as a result of ligand isomerization.[10] Thus 5 is uniquely accessible via metal atom methodology.

The possibility that a heteroatom in the chain connecting the two phenyl rings might serve as a template for the synthesis of bridged complex 1 was investigated. Under identical cocondensation conditions, chromium atoms (0.6 mmol)[5] were reacted with benzyl ether (19.7 mmol). The melted matrix was extracted with ethyl ether and filtered. The solvent was removed and the unreacted benzyl ether carefully sublimed off, leaving a yellow-green powder (mp 64-65°C) which exhibited the spectral properties expected for 7 (equation iii; 200 mg; 32%). ^{13}C nmr (C_6D_6): 139.4, 128.6, 127.8, 127.6 (uncomplexed arene ring), 88.8, 77.6, 75.2 (complexed arene ring), 73.4, 71.9 ($-CH_2-$) ppm; Mass spectrum: m/e 448 (17%), 250 (91), 158 (100); ^1H nmr (δ, C_6D_6): 7.10 (m, 5H), 4.32 (s, 4H), 4.15 (broad s, 5H) ppm. No significant quantities (< 0.002 mmol) of products arising from the deoxygenation of benzyl ether were detected.

In the same vein, chromium atoms (2.8 mmol)[5] were cocondensed with benzyl sulfide (45 mmol). Although trace amounts of a volatile yellow product were noted, the predominant reaction (equation v) was desulfurization to form bibenzyl (0.09 mmol) and trans-stilbene (0.17 mmol). This result is not surprising in light of oxygen abstraction reactions we have observed when metal atoms are cocondensed with organic compounds containing epoxy, nitro, nitroso, and amine oxide groupings.[11,12] Skell reported that cyclic thioethers are desulfurized and dehydrosulfurized when reacted with singlet carbon atoms,[13] and the desulfurization of thiophenes upon cocondensation with chromium and iron has been noted.[14]

Several attempts were made to convert 5 into 6. Upon pyrolysis, bis(arene)chromium compounds usually liberate ligand and deposit a chromium mirror.[15a] However, if the rate constant for the dissociation of the first 1,4-diphenylbutane from 5 were much faster than the second, "wrapping" to 6 might be observable. When 5 was heated neat at 215°C for 2 hr, however, only 1,4-diphenylbutane was formed (^{13}C nmr). Thus, either the second 1,4-diphenylbutane ligand falls off rapidly, or 6 itself is not stable to the pyrolysis conditions. Bis(arene)chromium compounds are also known to undergo $AlCl_3$-catalyzed arene exchange reactions at elevated temperatures.[15b] However, when 5 was fused with $AlCl_3$ at 124°C for 2 hr, (at which temperature 5 alone is stable), 1,4-diphenylbutane was the only product detectable by ^{13}C nmr.

The foregoing reactions clearly indicate that metal atoms exert no overwhelming template effect when reacted with polyphenylated ligands in neat matrices.[16] Our results stand in contrast to a communication by Nesmeyanov, Zaitseva, et.al., which appeared while this work was in progress.[17] Although experimental details are sparse, reaction of chromium vapor with a decane solution of 1,4-diphenylbutane was reported to yield 5 (29%), 6 (6%) and oligomeric and polymeric complexes (3: > 15%). These were oxidized to bis(arene)chromium iodides and characterized by tlc (R_f), microanalysis, and mass spectroscopy. In an attempt to duplicate these results, we cocondensed chromium atoms (1.76 mmol)[5] with 9.5 mmol 1,4-diphenylbutane in 20 ml hexadecane.

The crude reaction mixture was air oxidized and treated with KI as reported.[17] Significantly, *two* bis(arene)chromium iodides were present by tlc (acetone/ethanol 3:1, alumina plates, R_f 0.50 and 0.33) and subsequently separated by column chromatography. The less polar and preponderant (> 90%) product was the only one formed when chromium was condensed with neat 1,4-diphenylbutane and the reaction mixture oxidized by a parallel procedure. Its R_f and dec. pt. (154-156°C) correspond to those assigned the iodide of 5.[17] The minor product was isolated as yellow-orange crystals and its R_f and dec. pt. (156-158°C) agree with those assigned the iodide of 6.[17] We find the observation of substantial amounts of oligomeric and polymeric products by the Russians puzzling. Since their formation should *not* be enhanced in a diluted 1,4-diphenylbutane matrix, we believe the difference between their results and ours must be a consequence of reactor design or cocondensation conditions.

In conclusion, although syntheses of the iodide of the "wrapped" complex 6 have been achieved, it is evident that other strategies for the efficient formation of cyclophaes around metal *atoms* must be sought.[18] Several approaches are currently under active investigation.

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