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Preliminary communication

TETRAIRIDIUM CARBONYL CLUSTERS OF MONO- AND DI-OLEFINS

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Summary

The reactions of $NEt_4[Ir_4(CO)_{11}Br]$ (I) with mono- and di-olefins in the presence of $AgBF_4$ gave high yields (>90%) of $Ir_4(CO)_{11}$(olefin) (II) and $Ir_4(CO)_{10}(\eta^4$-diolefin) (III). Oxidation of $Ir_4(CO)_{11}L$ (L = PPh_3, $AsPh_3$) in the presence of an excess of diolefin by 1 eq. $ON(CH_3)_3$ gave the clusters $Ir_4(CO)_9L(\eta^4$-diolefin) (IV) and $Ir_4(CO)_7L(\eta^4$-diolefin$)_2$ (V). Sulphur dioxide quantitatively displaces the monoolefin ligand from II to give $Ir_4(CO)_9(\mu_2\text{-}CO)_2(\mu_2\text{-}SO_2)$, which is the first example of a tetrairidium—SO_2 cluster.

The development of the chemistry of $Ir_4(CO)_{12}$ is hampered by its near insolubility in all solvents, and CO substitution reactions are restricted to good donor ligands such as phosphines, arsines and isonitriles [1]. Thermal CO substitutions by olefins and polyolefins are complicated by dehydrogenation of the ligands and changes in nuclearity of the clusters. Well characterized tetrairidium clusters with diolefins are $Ir_4(CO)_{12-2x}(1,5\text{-COD})_x$ (COD = cyclooctadiene; x = 1,2,3) [2]. In view of their potential as catalysts, for which adjacent metal centers offer the possibility of cooperative reactivity, we started a systematic study of tetrairidium carbonyl clusters containing C=C bonds. The soluble anionic cluster $[Ir_4(CO)_{11}Br]^-$ [3] is ideally suited as a starting material for selective monosubstitution reactions, and many cluster compounds have recently been isolated from the reaction of $NEt_4[Ir_4(CO)_{11}Br]$ with mono- and bidentate phosphines and arsines [4]. We have found that similar replacements of the bromide ligand by olefins proceed readily in the presence of $AgBF_4$.

High yields (>90%) of yellow clusters of type II (Scheme 1) were obtained by route i, but the less stable ethylene cluster IIa tends to decompose in solu-

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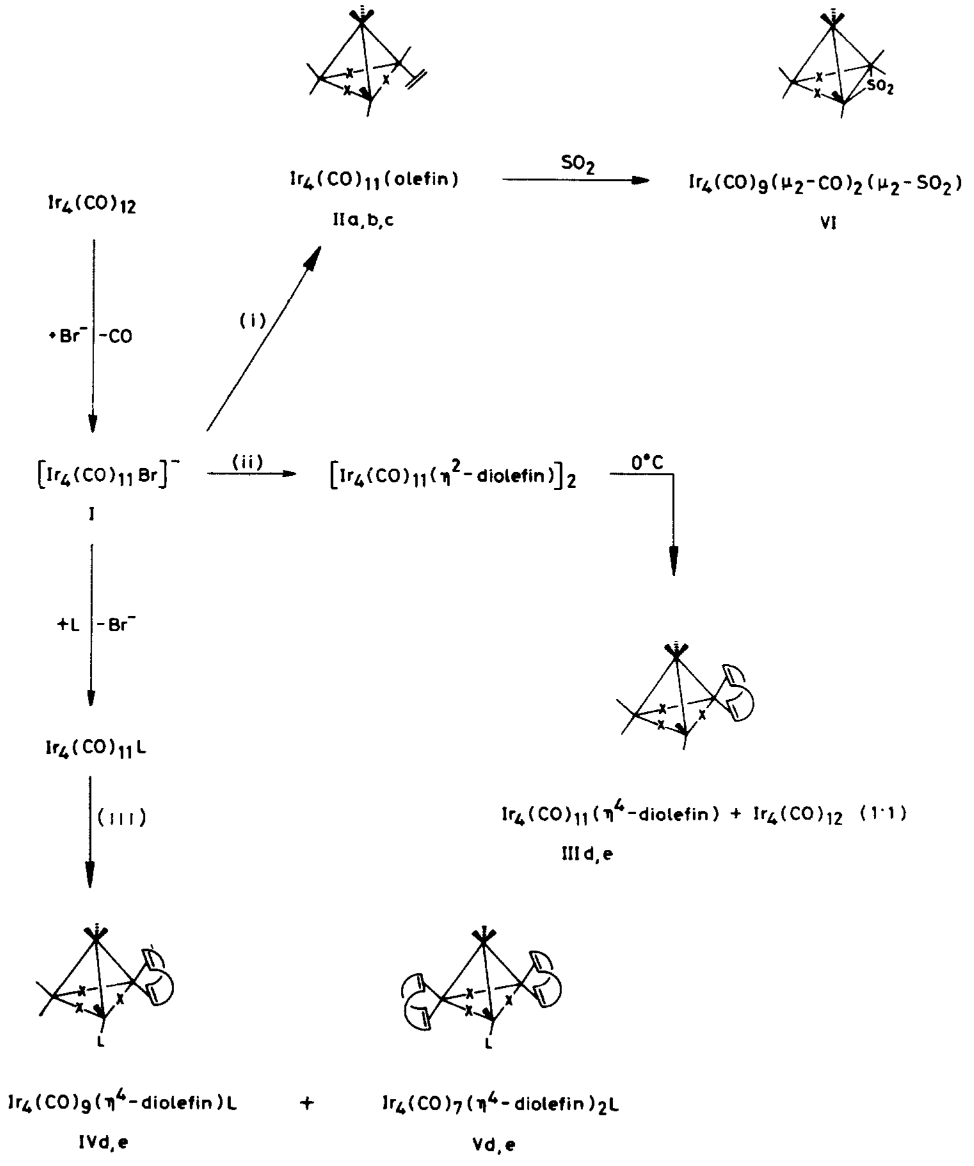

SCHEME 1. —X— = μ-CO; L = PPh_3; a = ethylene; b = norbornene; c = 5,6-dimethylidene-7-oxabicyclo-[2.2.1]hept-2-ene; d = 1,5-norbornadiene; e = 1,5-cyclooctadiene:
(i) + olefin in CH_2Cl_2 at −30°C; + $AgBF_4$ (1:1) (AgBr filtered)
(ii) + diolefin in CH_2Cl_2 at −10°C; + $AgBF_4$ (1:1) (AgBr filtered)
(iii) + excess diolefin; + $ON(CH_3)_3$ in THF at room temperature; TLC.

tion above −30°C in the absence of free ethylene. The higher stability of the clusters with strained olefins is in keeping with what is generally observed for complexes of nickel(0) [5], palladium(0) and platinum(0) [6].

Reaction ii with diolefins gave a yellow solution, presumably containing the bridged clusters $[Ir_4(CO)_{11}(\eta^2\text{-diolefin})]_2$ which cleanly disproportionate into $Ir_4(CO)_{12}$ (recycled) and $Ir_4(CO)_{10}(\eta^4\text{-diolefin})$ (IIId, IIIe). Oxidation (route iii) of $Ir_4(CO)_{11}L$ (L = PPh_3, $AsPh_3$) in the presence of an excess of diolefin by 1 eq. $ON(CH_3)_3$ gave a mixture of two clusters, IV and V, which were separated by preparative TLC.

The structures of I—V follow from their IR, ^1H, ^{13}C and ^{31}P NMR characteristics and from comparison with the corresponding $Ir_4(CO)_{11}L$ [7], $Ir_4(CO)_{10}L_2$ (L_2 = diarsine [8]; L = PPh_2CH_3 [9]) and $Ir_4(CO)_9L_3$ [10].

All the compounds show 3 IR bands characteristic of bridging CO's. The first substitution takes place preferentially at an axial site, and chelation on a radial site of the same metal center follows. The clusters IVd, IVe and Vd are non-fluxional and have L on an axial site. For Ve two isomers are obtained in a 3/1 ratio (L radial/L axial). The clusters II and III are fluxional at room temperature. The low-temperature ^1H and ^{13}C NMR spectra of IIId,e indicate that the mid-points of the two C=C bonds reside on a mirror plane containing the apical Ir atom and one basal μ-CO. Likewise in Vd,e, the two diolefins are related by a mirror place containing the apical Ir atom, L, and one basal μ-CO.

IIa: δ(H) (360 MHz, 230 K, $CDCl_3$): 3.55 ppm; coordination chemical shift $\Delta\delta = \delta(\text{ligand}) - \delta(\text{complex}) = 1.88$ ppm.

IIb: δ(H) (360 MHz, 230 K, $CDCl_3$): 4.05 br s, 2.82 br s, 1.69 m, 1.45 d, 1.19 d, 0.92 d; $J_{1,2} \simeq J_{1,3} = 1.2$ Hz, $J_{syn,anti} = 9.5$ Hz, $J_{sn,sx} = 8.5$ Hz; $\Delta\delta$ = 1.95 ppm. The magnitude of $J_{1,2}$ indicates that the C=C bond is coordinated through its *exo*-face [10]. δ(C) (90.55 MHz, 190 K, CD_2Cl_2) CO: 205.1, 195.5, 170.8, 170.1, 155.6, 155.5, 154.3 ppm, ratios 2/1/2/1/2/1/2.

IIId: δ(H) (360 MHz, 190 K, CD_2Cl_2): 4.49 br s (bridge heads), 4.61 br s (radial H—C=C), 3.95 br s (axial H—C=C), 1.15 dd; $J_{syn,anti} = 7$ Hz, other J's < 1 Hz.

IVd: δ(H) (360 MHz, 230 K, $CDCl_3$): 4.41, 4.18 br s (bridge heads), 4.24 t (H(2,3), radial), 3.74 t and 2.26 t (H(5,6), axial), 1.07 d and 0.97 d (H(7)); $J_{syn,anti} = 9.3$ Hz, $J_{2,3}$ and $J_{5,6}$ = 3.4—3.7 Hz. δ(C) (90.55 MHz, 190 K, CD_2Cl_2): 218.1 s, 207.2 s, 174.2 d ($^2J(P,C) = 5.7$ Hz), 170.8 s, 161.6 s, 159.0 d ($^3J(P,C) =$ 27.8 Hz with apical CO in pseudo-*trans* position), 158.7 s, 154.3 s. δ(P) (81 MHz, 220 K, CD_2Cl_2): −20.23 ppm relative to H_3PO_4 85%.

Vd: δ(H) (360 MHz, 230 K, $CDCl_3$): 4.49, 4.00 br s (bridge heads), 4.32, 4.03 dd (H(2,3), radial), 3.71, 2.36 dd (H(5,6), axial), 1.00 and 0.91 d (H(7)); $J_{syn,anti} = 9.2$ Hz, $J_{2,3}$ and $J_{5,6}$ 3.3—3.7 Hz. δ(P) (300 K, $CDCl_3$): —27.68 ppm.

Carbon monoxide displaces the C=C bond of II and III to give $Ir_4(CO)_{12}$ and of IV and V giving $Ir_4(CO)_{11}L$. Sulfur dioxide quantitatively displaces the mono-olefin of II to give $Ir_4(CO)_9(\mu_2\text{-}CO)_2(\mu_2\text{-}SO_2)$ (VI), which is the first example of a tetrairidium-SO_2 cluster.

VI: IR (Nujol): 2118 w, 2090 vs, 2045 s, 1912 s, 1865 vs, 1264 s, 1093 vs. δ(C) (90.55 MHz, 190 K, CD_2Cl_2): 190.6, 169.3, 165.7, 155.6, 155.3, 151.6 and 149.3, ratios 2/1/2/1/2/2/1.

The fluxional behaviour and the reactivity of these compounds are under study.

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