Journal of Organometallic Chemistry, 182 (1979) C5—C10

Preliminary communication

METAL-OLEFIN BONDING. GROUP VI METAL CARBONYL COMPLEXES CONTAINING THE LIGANDS 1,6-BIS(DIPHENYLPHOSPHINO)-*TRANS*-HEX-3-ENE AND 1,6-BIS(DIPHENYLARSINO)-*TRANS*-HEX-3-ENE. THE CRYSTAL AND MOLECULAR X-RAY STRUCTURE OF TRICARBONYL-1,6-BIS(DIPHENYPHOSPHINO)-*TRANS*-HEX-3-ENEMOLYBDENUM(O).

GEORGE R. CLARK and CATHERINE M. COCHRANE

Department of Chemistry, University of Auckland, Auckland (New Zealand)

PETER W. CLARK

Department of Chemistry, University of Queensland, Brisbane 4067 (Australia)

ALAN J. JONES and PETER HANISCH

The National NMR Centre, Australian National University, Canberra 2600 (Australia)

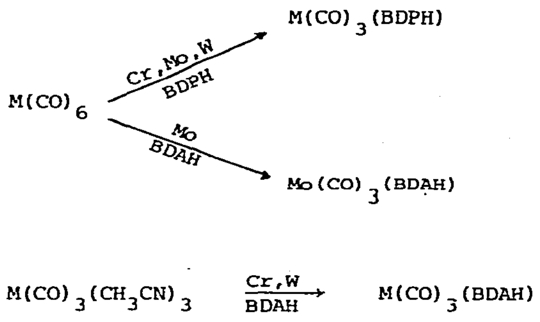
(Received September 27th, 1979)

Summary

The title compounds have been prepared, and characterised by ^1H and ^{13}C N.M.R. spectroscopy. The X-ray structure of one of the molybdenum complexes has been determined.

It has been shown previously that the ligands 1,6-bis-(diphenylphosphino)-*trans*-hex-3-ene (BDPH) and 1,6-bis(diphenyl-arsino)-*trans*-hex-3-ene (BDAH) form square-planar rhodium(I) and iridium(I) and octahedral rhodium(III) and iridium(III) complexes of the general formula MX(BDPH), MX(BDAH), M = Rh or Ir, X = halide; and M(XY)Cl(BDPH) where M = Rh, XY = Cl_2 or Br_2, or M = Ir, XY = H_2, Cl_2, HCl or Br_2 respectively [1-3]. Of particular importance has been the orientation of the olefin with respect to the plane containing the metal, the two phosphorus atoms, and the atom *trans* to the olefin. In the complexes IrCl(BDPH), $IrCl_3$(BDPH) and IrH_2Cl(BDPH), this tilt angle is 79.4°, 28.1° and 40.2° respectively.

The ligands 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene (BDPH) and 1,6-bis(diphenylarsino)-*trans*-hex-3-ene (BDAH) react with the metal hexacarbonyl compounds, $M(CO)_6$, M = Cr, Mo or W, or the acetonitrile substituted compounds (see Scheme 1) to form the corresponding complexes $M(CO)_3$(BDPH) and $M(CO)_3$(BDAH). BDPH reacted smoothly with the Group VI metal hexacarbonyl complexes displacing three carbon monoxide ligands. The molybdenum compound $Mo(CO)_3$(BDAH) was readily prepared from $Mo(CO)_6$ and BDAH, but the chromium and tungsten complexes $Cr(CO)_3$(BDAH) and $W(CO)_3$(BDAH) were best prepared from the corresponding tris(acetonitrile)metaltricarbonyl compounds. The tungsten compound $W(CO)_3$(BDAH) could not be prepared from $W(CO)_6$ and the ligand. All the complexes were stable in the solid



SCHEME 1

Preparation of the complexes $M(CO)_3$(BDPH) and $M(CO)_3$(BDAH).

state and, with the exception of $Cr(CO)_3(BDAH)$, were stable in solution. $Cr(CO)_3(BDAH)$ decomposed in solution when left to stand for extended periods, and we were unable to obtain its ^{13}C nuclear magnetic resonance spectrum.

The upfield shift of the olefin in the ^1H N.M.R. spectra in the complexes compared to the ligand is clear indication that the olefin is bonded to the metal (see Table) [4]. The proton-decoupled ^{13}C N.M.R. spectra are easily interpreted, and in many respects are similar to the spectra of the rhodium and iridium complexes containing these ligands. In all cases, the ^{13}C N.M.R. spectra consisted of a phenyl region, an olefinic resonance and two alkyl resonances. The coordination induced shifts $\Delta\delta C$ in the chromium complex $Cr(CO)_3(BDPH)$, in the molybdenum complexes $Mo(CO)_3(BDPH)$ and $Mo(CO)_3(BDAH)$, and in the tungsten complexes $W(CO)_3(BDPH)$ and $W(CO)_3(BDAH)$ are 35.0, 31.0, 31.8, 38.4 and 40.0 ppm, respectively. The $\Delta\delta C$ values for the

TABLE 1

SELECTED ^1H AND ^{13}C N.M.R. DATA[a] FOR THE COMPLEXES $M(CO)_3(BDPH)$ AND $M(CO)_3(BDAH)$, M = Cr, Mo, W.

Compound	δH (olefin)	δC (olefin)[b]	ΔδC (olefin)[b]
BDPH[d]	5.50	130.9	
$Cr(CO)_3(BDPH)$	∿4.60	95.9	35.0
$Mo(CO)_3(BDPH)$	4.75	99.9	31.0
$W(CO)_3(BDPH)$	4.34	92.5	38.4
BDAH[d]	5.45	131.3	
$Cr(CO)_3(BDAH)$	4.60	[c]	[c]
$Mo(CO)_3(BDAH)$	4.61	99.5	31.8
$W(CO)_3(BDAH)$	4.21	91.3	40.0

[a] All complexes were dissolved in CD_2Cl_2, the spectra were recorded at ambient temperatures. [b] ^1H and ^{13}C chemical shifts in ppm relative to TMS, δ = 0. [c] ^{13}C N.M.R. not recorded due to decomposition in solution. [d] Ref. 5.

molybdenum(O) d^6 octahedral complex, $Mo(CO)_3(BDPH)$, and for the tungsten(O) d^6 octahedral complex $W(CO)_3(BDPH)$, are greater than those for the corresponding rhodium(III) d^6 octahedral complex $RhCl_3(BDPH)$ ($\Delta\delta C$ = 15.0 ppm) and the iridium(III) d^6 octahedral complex $IrCl_3(BDPH)$ ($\Delta\delta C$ = 30.5 ppm) respectively [5].

Changes in ^{13}C shifts in olefins induced by complexation with metals have been the subject of numerous "theoretical" interpretations[6]. We would hope that data for a range of metals would reflect periodic table trends and indeed the present $\Delta\delta C$ comparison between d^6 M(III) and d^6 M(O) complexes appear to do so. We emphasise that the magnitude of the induced shifts are clearly a complex function of M-C distance, stereochemistry, oxidation state and olefin orientation [5]. While we condone the view expressed by Waugh that hope of a qualitative theoretical interpretation in terms of the nature of the chemical bonding in these substances should be forthcoming, we hasten to add that at present there is no comprehensive view [6]. Data for the same ligands over a wide range of metals should provide a sound basis for theoretical interpretation. Presently we suggest that the coordination induced shifts for the metals we have studied appear to add credence to the Dewar-Chatt-Duncanson model of metal-olefin bonding provided oxidation state and stereochemistry of the complexes are considered.

In order to further investigate the detailed structures of metal-olefin complexes, we have determined the crystal structure of $Mo(CO)_3(BDPH)$. The lemon-coloured crystals are orthorhombic, space group *Pbca* with 8 molecules in a unit cell of dimensions a = 16.991(2) b = 20.073(4) c = 17.333(2) Å. At the present stage of least-squares refinement only the molybdenum and phosphorus atoms have been assigned anisotropic thermal parameters and absorption corrections have still to be applied. The discrepancy index, R, is 0.08.

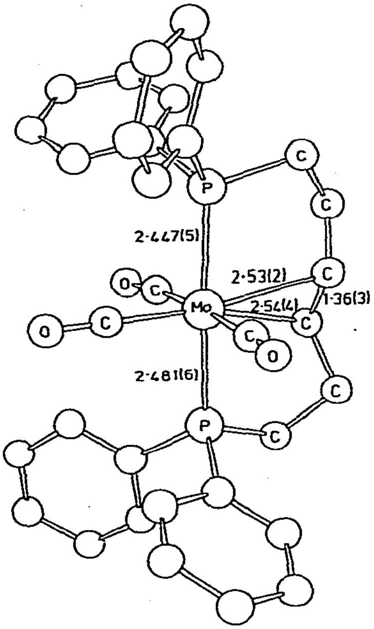


Figure. The coordination geometry in Mo(CO)$_3$(BDPH).

The overall geometry is shown in the figure. The metal-olefin interaction is characterised by long Mo-C bonds and a short C=C bond, presumably because the olefin competes less successfully than the three carbonyl ligands for π-electron density from the metal. Concomitant with a low extent of metal-π* back-bonding is a relaxation of the necessity of the olefin to adopt a specific orientation either perpendicular or parallel to the Mo P(1) P(2) C(8) plane, and, as was found in the Ir(III) complexes cited earlier [2,3] the olefin adopts an intermediate orientation at an angle of 31.8° to the above plane. The symmetrical metal-olefin bonding is consistent with the presence of only one olefin ^{13}C N.M.R. signal.

References

1 P.W. Clark, J. Organometal. Chem., 137(1977)235.

2 G.R. Clark, P.W. Clark, A.J. Jones and D.R. Russell, J. Organometal. Chem., 166(1979)109.

3 G.R. Clark, P.W. Clark and K. Marsden, J. Organometal. Chem., 173(1979)231.

4 M.A. Bennett, Chem. Reviews, 62(1962)611.

5 P.W. Clark, P. Hanisch and A.J. Jones, Inorg. Chem., 18 (1979) 2067.

6 M.M. Maricq, J.S. Waugh, J.L. Fletcher and M.J. McGlinchey, J. Amer. Chem. Soc., 100(1978)6902, and references therein.