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η^3-Cyclopropenyl Is Isolobal with NO, but Not with η^3-Propenyl (Allyl): Evidence from Conformational Preferences and Rotational Barriers in Alkene and Alkyne Complexes of Iridium

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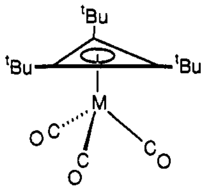
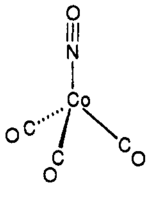
Summary: $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ *reacts with tetrafluoroethylene or 2-butyne to afford trigonally coordinated monocarbonyl alkene or alkyne complexes that are fluxional with respect to rotation of the cyclopropenyl and alkene or alkyne ligands. The ground state conformation of the alkyne ligand is shown to be the more sterically hindered one, and the isolobal relationship between cyclopropenyl and NO is used to explain this preferred conformation. The* C_2F_4 *complex reacts with* PMe_3 *to give a 4-coordinate adduct in which the barrier to propeller rotation of* C_2F_4 *is low, in contrast with the significantly higher barrier previously observed for an analogous* η^3*-propenyl (allyl) complex. Differences between* η^3*-cyclopropenyl and* η^3*-propenyl are discussed using the isolobal analogy.*

η^3-Cyclopropenyl and η^3-propenyl (allyl) are the simplest three-carbon fragments capable of ligating to transition metal centers. Each presents to a metal an array of three molecular orbitals arising from its endogenous π-system; in allyl each orbital is of different energy while for cyclopropenyl the two highest energy orbitals are degenerate. In many previous papers we have chosen to consider η^3-cyclopropenyl as a formally monoanionic 4-electron donor, as is often assumed for its acyclic analogue.[1] For electron counting purposes it is usually irrelevant whether these ligands are considered as cationic, 2-electron donors, anionic 4-electron donors, or neutral 3-electron donors, but the predictions of the isolobal analogy[2] can differ significantly. For example, if allyl is considered as a monocationic 2-electron donor, the 16-electron fragment $[Ir(\eta^3\text{-allyl})(CO)_2]$ is isolobal with $[Ir(CO)_3]^-$, a d^{10} ML_3 fragment; if allyl is a monoanionic 4-electron donor, the same complex is isolobal with $[Ir(CO)_4]^+$, a d^8 ML_4 fragment.

Recently, the intimate nature of the orbital interactions between a cyclopropenyl ligand and a transition metal fragment have been probed using UV photoelectron spectroscopy.[3] A detailed study of complexes 1 and 2 concluded that the tri-*tert*-butylcyclopropenyl ligand is best described as acting as a 2-electron monocationic donor, isolobal with the linear NO ligand in complex 3, although cyclopropenyl is an understandably poorer π-acceptor than is NO. These results indicate that, like 3, complexes 1 and 2 are best considered as tetrahedral d^{10} complexes of the metal in a formal oxidation state of −1. This result caused us to contemplate (a) whether further chemistry and ligation at the metal center predicted by the formal isolobal relationship between NO and the tri-*tert*-butylcyclopropenyl ligand might be outweighed sterically by the extreme bulk of the latter and (b) whether cyclopropenyl and allyl might indeed be quite dissimilar ligands. Here we present evidence that η^3-tri-*tert*-butylcyclopropenyl imposes bonding characteristics on a metal fragment identical to those expected for the sterically svelte NO, without overwhelming steric attenuation by the zaftig nature of the former ligand, and that these characteristics are significantly different from those imposed by the acyclic η^3-allyl ligand.



1 M = Ir
2 M = Co



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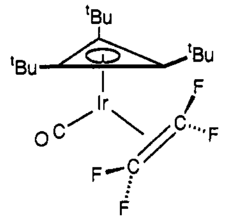
Reaction of the tricarbonyl complex **1**[3] with the CO abstracting agent *N*-methylmorpholine *N*-oxide (NMO), followed by addition of tetrafluoroethylene, afforded the bright yellow, air stable, monocarbonyl complex **4** (37%).[4]



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[®] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

[1] Ditchfield, R.; Hughes, R. P.; Tucker, D. S.; Bierwagen, E. P.; Robbins, J.; Robinson, D. J.; Zakutansky, J. *Organometallics* **1993**, *12*, 2258 and references cited therein.

[2] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[3] Lichtenberger, D. L.; Hoppe, M. L.; Subramanian, L.; Kober, E. M.; Hughes, R. P.; Hubbard, J. L.; Tucker, D. S. *Organometallics* **1993**, *12*, 2025.

[4] NMO (0.027 g, 0.232 mmol) was added to a cold (−60 °C), colorless solution of 1 (0.107 g, 0.221 mmol) in THF (20 mL). The Schlenk flask was evacuated and then filled with C_2F_4. The mixture was warmed to ambient temperature and stirred overnight to give a bright yellow solution. Solvent removal and chromatography [Florisil; 1 × 12 cm, −70 °C, eluting first with hexanes (300 mL) followed by diethyl ether (60 mL)] afforded recovered starting material 1 (30%) and product 4 (0.040 g, 37%); mp 102 °C dec: IR (hexanes) ν_{CO} 2026 cm^{-1}; ^{1}H NMR (toluene-d_8, −80 °C) δ 0.99 (s); $^{13}C\{^1H\}$ NMR (^{13}CO enriched sample[5]) (toluene-d_8, −80 °C) 181.98 (pentuplet, $^3J_{CF}$ = 10 Hz, CO), 150.80 ($C_3{}^tBu_3$), 89.52 (t, C_2F_4, $^1J_{CF}$ = 311 Hz), 35.75 (CMe_3), 29.90 (CH_3); $^{19}F\{^1H\}$ NMR (C_6D_6; 22 °C) δ −106.20 (s); $^{19}F\{^1H\}$ NMR (toluene-d_8, −80 °C) δ −100.4 (s, br), −103.0 (s, br). Anal. Calcd for $C_{18}H_{27}F_4OIr$: C, 40.98; H, 5.16. Found: C, 40.85; H, 4.97.

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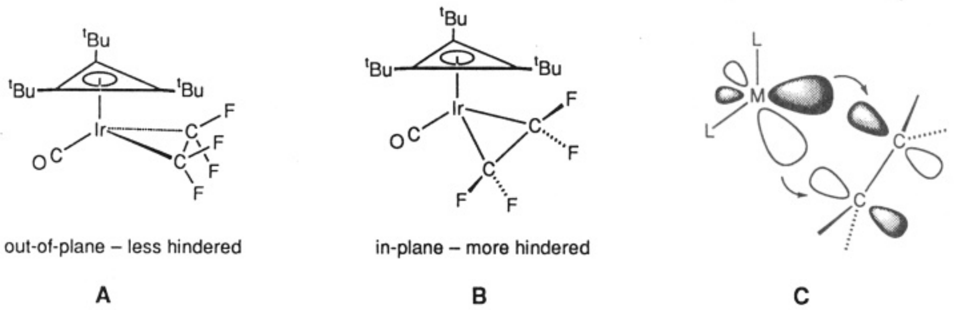


out-of-plane – less hindered

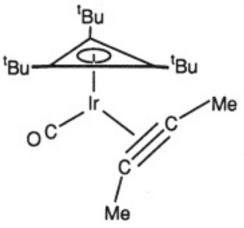
in-plane – more hindered

Figure 1. (A) Out-of-plane conformation of olefin. (B) In-plane conformation of olefin. (C) Interaction between the in-plane molecular orbital of the ML_2 fragment with olefin π^*. The trigonal plane of coordination is defined by the three vectors from iridium to the C_3 centroid, the CO ligand, and the midpoint of the C=C bond of the olefin, and lies in the plane of the paper.

Attempts to prepare the corresponding ethylene analogue were unsuccessful. As expected, the IR spectrum of 4 showed a single sharp $\nu(^{12}CO)$ at 2026 cm^{-1}. Repetition of this procedure using ^{13}CO enriched 1[5] afforded a sample of isotopically enriched 4 [$\nu(^{13}CO)$ 1976 cm^{-1}]. The ^1H and ^{19}F NMR spectra of 4 showed a single environment for the three *tert*-butyl groups and for all four fluorine atoms, consistent with fast rotation of both the cyclopropenyl and tetrafluoroethylene ligands about their respective metal–ligand axes at room temperature. The room temperature $^{13}C\{^1H\}$ NMR spectrum was also consistent with a highly fluxional complex, with single environments being observed for each of the cyclopropenyl ring carbon atoms, the *tert*-butyl groups, and the C_2F_4 carbons; the resonance for ^{13}CO appears as a binomial quintet due to coupling to four equivalent ^{19}F atoms. The barriers to cyclopropenyl and olefin rotation in this complex are clearly low; no decoalescence was observed in the ^{13}C or ^1H NMR spectra on cooling to −80 °C, although the ^{19}F NMR spectrum did decoalesce to two very broad peaks at this temperature. Line shape analysis[6] of the latter variable temperature behavior affords a value of $\Delta G^{\ddagger}$ for C_2F_4 rotation of 29 ± 1 kJ·mol^{-1}.[7]

The low temperature spectra of 4 are inconclusive in defining the preferred ground state conformation of the olefin ligand with respect to the trigonal plane of coordination, as defined by the three vectors from iridium to the C_3 centroid, the CO ligand, and the midpoint of the C=C bond of the olefin. Two ^{19}F environments are expected for either the out-of-plane conformation (Figure 1A) or in-plane conformation (Figure 1B). The single ^{13}C resonance observed for the C_2F_4 ligand at low temperatures is consistent with either conformation if olefin rotation is fast, or with the out-of-plane conformation if rotation is slow. Repeated attempts to obtain crystals suitable for X-ray analysis proved fruitless.

Fortunately, this conformational ambiguity is absent in the corresponding 2-butyne complex 5, prepared from reaction of 1 with NMO, followed by addition of the alkyne.[8] The ^1H NMR spectrum of 5 shows rapid rotation for the cyclopropenyl ligand at room temperature and below, but the single methyl resonance for the 2-butyne ligand observed at ambient temperature decoalesces into two quartets at −40 °C, with a $\Delta G^{\ddagger}$ for alkyne rotation of 58 ± 1 kJ·mol^{-1}. This observation clearly demonstrates that the preferred alkyne conformation in 5 is that in which the C–C axis lies in the sterically less preferable in-plane orientation, as shown. We assume that the same conformational preference (Figure 1B) holds for 4.



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The isolobal analogy is a powerful tool in explaining conformational preferences of ligands bound to transition metal centers.[2] The isolobal relationship between $C_3{}^tBu_3$ and NO[3] requires the corresponding relationship between the [Ir(CO)($^tBu_3C_3$)], [Ir(CO)(NO)], and [Pt(CO)$_2$] fragments; i.e. all are bent d^{10} ML_2 fragments. Theoretical analyses of the bent d^{10} ML_2 fragment indicate that the principal orbital responsible for back-bonding into an olefin or alkyne π^* MO lies in the trigonal plane (Figure 1C).[9] Complexes 4 and 5 are therefore structurally related to their well-known trigonal analogues [$ML_2(C_2)$] [M = Ni, Pd, Pt; L = tertiary phosphine; C_2 = olefin or alkyne]. While the steric bulk of the tri-*tert*-butylcyclopropenyl ligand is clearly insufficient to overcome this orbitally controlled ground state preference, it is noteworthy that the barriers to olefin and alkyne rotation in 4 and 5 are considerably lower than normally observed[10] in trigonal d^{10} systems, indicating that some steric destabilization of the in-plane ground state relative to the out-of-plane conformation may be present in these compounds.

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(5) Isotopically enriched samples were prepared by treating natural abundance samples of 1 with NMO, followed by exposing the solution to ^{13}CO. Subsequent reaction with NMO and C_2F_4 afforded enriched samples of 4.[4]

(6) The original version of the dynamic NMR simulation program was written by: Kleier, D. A.; Binsch, G. *J. Magn. Reson.* **1970**, *3*, 146–160; Program 165, Quantum Chemistry Program Exchange, Indiana University. Modifications are described in: Bushweller, C. H.; Bhat, G.; Lentendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65–73.

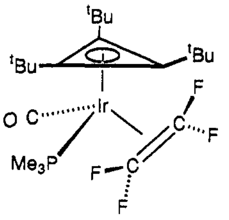
(7) This is a remarkably low activation barrier for propeller rotation of C_2F_4. See: Curnow, O. J.; Hughes, R. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 3153. Curnow, O. J.; Hughes, R. P.; Mairs, E. N.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3102.

(8) 5 (40%): ν_{co} (hexanes) 1985 cm^{-1}; ^1H NMR (toluene-d_8, −40 °C) δ 2.98 (q, 3H, Me, $^5J_{HH}$ = 1 Hz), 2.51 (q, 3H, Me, $^5J_{HH}$ = 1 Hz), 1.25 (s, 27H, ^tBu). Samples of 5 were unstable at room temperature and were invariably contaminated with traces of 1. Satisfactory microanalysis results could not be obtained.

(9) (a) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (b) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, U.K., 1983; Vol. 3, Chapter 19, p 1.

(10) Mann, B. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, U.K., 1983; Vol. 3, Chapter 20, p 89.

Compound **4** reacts with PMe_3 to afford the adduct **6**.[11]



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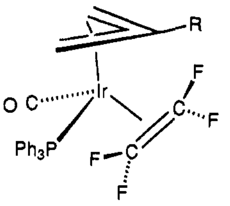

7 R = H, Me

In the latter complex the barrier to rotation of the $^tBu_3C_3$ ligand is similar ($\Delta G^{\ddagger} = 77 \pm 1$ kJ·mol^{-1}) to those observed in tetrahedral analogues [Ir($^tBu_3C_3$)(CO)$_2$L] (L = PR_3),[12] while the barrier for propeller rotation of the C_2F_4 ligand is similar ($\Delta G^{\ddagger} = 60 \pm 1$ kJ·mol^{-1}) to those reported for d^6 complexes such as [Ru(C_5Me_5)(acac)(C_2F_4)].[7,13] A comparison with the known allylic complexes **7** reveals a dramatic difference in the barrier for rotation of the C_2F_4 ligand, which is rigid on the NMR time scale in the latter complexes.[14] Treatment of $^tBu_3C_3$ in **6** as a cationic 2-electron donor imposes the isolobal relationship between [Ir($^tBu_3C_3$)(CO)(PMe_3)] and a C_{3v}[Ir(CO)$_3$]$^-$; an olefin bound to this d^{10} fragment is predicted to have a low rotation barrier.[9] In contrast, treatment of the allyl ligand in **7** as an anionic 4-electron donor requires the isolobal relationship between [Ir(C_3H_5)(CO)(PPh_3)] and a C_{2v}[Ir(CO)$_4$]$^+$ fragment for which a significantly higher barrier for rotation of a ligated olefin is predicted.[9]

These observations provide support for the idea that the isolobal relationship between NO and cyclopropenyl is a legitimate one for predicting conformational preferences for the binding of olefins and alkynes to metal fragments bearing these ligands, even in circumstances of a considerable steric bias. They also suggest intriguingly that cyclopropenyl and allyl ligands impose significantly different properties on a metal fragment to which they are bound. Further studies of the chemistry of these and related complexes is in progress.

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(11) **6** (97%): mp 98 °C dec; IR (hexanes) $\nu(^{12}CO)$ 1986 cm^{-1}; $\nu(^{13}CO)$ 1945 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.31 (s, 9H, ^{t}Bu), 1.21 (s, 9H, ^{t}Bu), 1.18 (s, 9H, ^{t}Bu) 1.04 (d, 9H, PMe_3, $^2J_{PH} = 9$ Hz), coalescence occurs on warming; $^{13}C\{^1H\}$NMR (toluene-d_8) δ 181.22 (t, CO, $^3J_{CF} = 9$ Hz), 97.94 (dt, C_2F_4, $^2J_{CP} = 5$ Hz, $^1J_{CF} = 320$ Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −57.88 (tt, $^3J_{PF}$ = 55, Hz, $^3J_{PF} = 10$ Hz); $^{19}F\{^1H\}$ NMR (toluene-d_8, −80 °C) δ −100.97 (ddd, $^2J_{gem} = 166$ Hz, $^3J_{trans} = -39$ Hz, $^3J_{PF} = 50$ Hz), −111.85 (dd, $^2J_{gem} = 166$ Hz, $^3J_{trans} = -36$ Hz), −116.93 (ddd, $^2J_{gem} = 177$ Hz, $^3J_{trans} = -39$ Hz, $^3J_{PF} = 57$ Hz), −124.12 (dd, $^2J_{gem} = 177$ Hz, $^3J_{trans} = -36$ Hz). Anal. Calcd for $C_{21}H_{36}F_4IrOP$: C, 41.78; H, 6.01. Found: C, 41.82; H, 5.99.

(12) Hughes, R. P.; Tucker, D. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3069.

(13) The lowest barriers for propeller rotation should be found in complexes of olefins ligated to d^6 ML_5 (C_{4v}) and d^{10} ML_3 (C_{3v}) fragments.[9] In the ^{19}F NMR spectrum of **6** site exchanged induced coalescence occurs between mutually trans pairs of fluorines. This is consistent only with propeller rotation and not with any dissociation/recombination mechanism.

(14) Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1975**, 1128.