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Rhodium and iridium complexes with 2-(diphenylphosphanyl)anilido ligands: reactions with phenylacetylene and dimethyl acetylenedicarboxylate †

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Treatment of [Ir(CO)(PPh$_3$)('PNMe')] ('PNMe' = 2-Ph$_2$PC$_6$H$_4$NMe$^-$) with phenylacetylene resulted in oxidative addition and opening of the chelate ring to afford mono- and bis-(alkynyl) derivatives, [IrH(C≡CPh)(CO)(PPh$_3$)('PNMe')] **1** and [IrH(C≡CPh)$_2$(CO)(PPh$_3$)(η^1-'PN(Me)H')] **2**, respectively. Complex **2** exists as two isomers with *trans*-located phosphane ligands and *cis*- or *trans*-coordinated alkynyl groups. The minimum values of the spin–lattice relaxation times, $T_1^{(\mathrm{min})}$, observed for the hydride ligands of the two isomers ruled out the possibility of short IrH···HN contacts in **2**. Combination of [Ir(CO)(PPh$_3$)('PNMe')] with dimethyl acetylenedicarboxylate (dmad) gave the irida(III)cyclopropene-like complex [Ir{C$_2$(CO$_2$Me)$_2$}(CO)(PPh$_3$)('PNMe')] **3** as the expected 1 : 1 adduct. In contrast, [Rh(CO)(PPh$_3$)('PNMe')] and dmad interacted by insertion of the activated alkyne into the Rh–N bond, forming the seven-membered metallaheterocycle [Rh{C(CO$_2$Me)=C(CO$_2$Me)N(Me)C$_6$H$_4$PPh$_2$-2}(CO)(PPh$_3$)] **4**. [Ir(CO)(PPh$_3$)('PNH')] ('PNH' = 2-Ph$_2$PC$_6$H$_4$NH$^-$) and dmad reacted to initially produce a mixture of metallacyclic [Ir{C$_2$(CO$_2$Me)$_2$}(CO)(PPh$_3$)('PNH')] **5** and unchanged starting materials. Subsequent treatment with methanol resulted in the formation of the iridium(III) complex [Ir{C(O)OMe}{C(CO$_2$Me)=CH[C(O)OMe]}(PPh$_3$)('PNH')] **6**, which X-ray crystallography showed to contain a chelating vinyl ligand featuring substantial carbenoid character.

Introduction

During the last few years we have been investigating some aspects of the chelation of bidentate 2-(diphenylphosphanyl)-aniline and -phenol ligands 2-Ph$_2$PC$_6$H$_4$XH (X = NH, NMe, O), both in their neutral ('PXH') and deprotonated ('PX') forms, in particular with respect to the reactivity of their tungsten, rhodium, and iridium complexes towards Brønsted acids.[1] Following these studies, we have turned our attention to reactions of terminal and internal alkynes, such as phenylacetylene and dimethyl acetylenedicarboxylate, with Vaska-type rhodium and iridium complexes containing anionic 2-(diphenylphosphanyl)anilido or 2-(diphenylphosphanyl)-*N*-methylanilido ligands, 2-Ph$_2$PC$_6$H$_4$NH$^-$ ('PNH') and 2-Ph$_2$PC$_6$H$_4$NMe$^-$ ('PNMe'), respectively.[1b]

Prior to this work, low-valent iridium compounds possessing non-chelating amido ligands, *e.g.*, [Ir(NHBu^t)(CO)(PEt$_3$)$_2$], have been reported to react with PhC≡CH by protonation of the amide function and oxidative addition of the alkyne to give hydrido bis(alkynyl)iridium(III) derivatives.[2] With the chelate complexes [Ir(CO)(PPh$_3$)('PNR')] (R = H, Me) as starting materials a similar reaction sequence should allow one to find access to ring-opened products of the type [IrH(C≡CH)$_2$(CO)(PPh$_3$)('PN(R)H')], resembling the previously reported hydridodichloro derivatives [IrHCl$_2$(CO)(PPh$_3$)(η^1-PN(Me)H')][1b] and [IrHCl$_2$(CO)(PPh$_3$)(η^1-'POH')],[1c] whose significance arises from the observation that they exist as Ir–'PN(Me)H' and Ir–'POH' rotamers stabilized not only by "classical" intramolecular IrCl···HN or IrCl···HO hydrogen bonds but also by "non-classical"[3–5] IrH$^{\delta-}$···$^{\delta-}$HO interactions. Reactions occurring between the chelated anilido complexes [M(CO)(PPh$_3$)('PNR')] (M = Rh, Ir; R = H, Me) and the MeO$_2$CC≡CCO$_2$Me ligand have attracted our interest because combination of the more electron-rich amide complexes of the late transition metals with alkynes bearing electron-withdrawing substituents has proved to be a suitable method for facile C–N bond making by addition of the metal–amide function across the –C≡C– triple bond of the unsaturated molecule.[6]

Results and discussion

Reactions with phenylacetylene

Both the rhodium complexes [Rh(CO)(PPh$_3$)('PNR')], where R = H or Me, and the iridium compound [Ir(CO)(PPh$_3$)('PNH')] proved to be completely unreactive towards PhC≡CH, even if treated with the alkyne in high excess at elevated temperature. In a similar way, the more metal-basic 2-(diphenylphosphanyl)-*N*-methylanilidoiridium(I) derivative [Ir(CO)(PPh$_3$)('PNMe')] underwent only sluggish oxidative C–H addition with formation of [IrH(C≡CPh)(CO)(PPh$_3$)('PNMe')] **1**, requiring five or more equivalents of phenylacetylene in toluene at 70 °C. The overall geometry of **1** shown above was confirmed by spectral data. In particular, the ^{31}P-{^{1}H} NMR spectrum of **1** consists of two AB doublets at δ −7.21 and 3.03, each split by 333.2 Hz, and the proton NMR contains an IrH triplet which shows equal *cis* coupling (14.8 Hz) to the two ^{31}P nuclei and has a chemical shift, δ −8.88, that appears to be characteristic of the presence of *trans*-H–Ir–CO units in carbonyl hydrido complexes of the general type [IrH(X)(Y)(CO)(PR$_3$)$_2$].[7–9]

Under the conditions chosen for the PhC≡CH reaction, the formation of **1** was accompanied by the ring-opened hydrido bis(alkynyl) complex [IrH(C≡CPh)$_2$(CO)(PPh$_3$)(η^1-'PN(Me)H')] **2** as a minor product which we were unable to separate from **1**, even after repeated attempts at purification using fractional crystallization or chromatography; product ratio **1**/**2** *ca.* 7 : 3 (from ^{31}P NMR). It is not clear whether **2** results from **1** by

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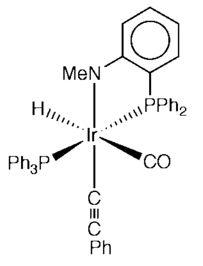
† Coordination chemistry of functional phosphanes. Part 9.[1a] Dedicated to Professor Dr W.-P. Fehlhammer on the occasion of his 60th birthday.
Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3935/



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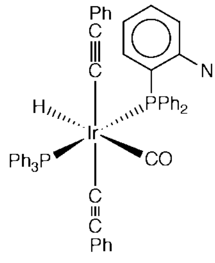
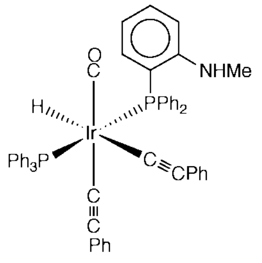


2a



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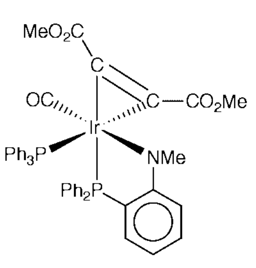

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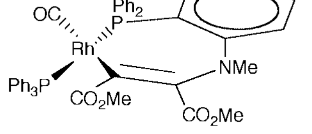

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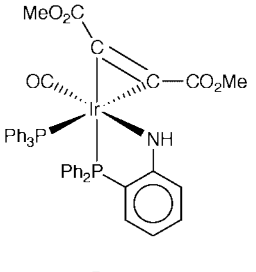

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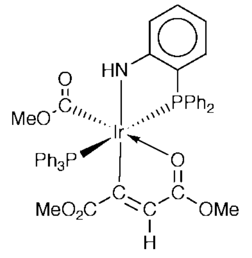

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protonation of the amide function, followed by dissociation of the Ir–N(Me)H bond and coordination of an additional alkynyl ligand, or is formed in competition with **1** directly from the [Ir(CO)(PPh$_3$)('PNMe')] starting complex by protolytic cleavage of the Ir–N bond, which would produce the monoalkynyl derivative [Ir(C≡CPh)(CO)(PPh$_3$)(η^1-'PN(Me)-H')] as an initial intermediate, prone to coordinate a second equivalent of PhC≡CH by oxidative addition. Two isomers, **2a** and **2b**, with separate IrH, NCH$_3$, and NH signals are seen for CDCl$_3$ solutions of **2**; **2a**: δ_H −9.11 [1 H, t, *cis*-^2J(PH) 15.6 Hz, IrH], 2.55 [3 H, d, ^3J(HH) 4.8 Hz, NCH$_3$] and 5.42 [1 H, q (br), NH]; **2b**: δ_H −9.48 [1 H, t, *cis*-^2J(PH) 16.8 Hz, IrH], 2.23 [3 H, d, ^3J(HH) 4.9 Hz, NCH$_3$] and 5.09 [1 H, q (br), NH]; isomeric distribution as estimated by ^{31}P NMR: **2a**, ≈80%; **2b**, ≈20%. In contrast to the formally analogous compounds [IrHCl$_2$(CO)-(PPh$_3$)(η^1-'PN(Me)H')] and [IrHCl$_2$(CO)(PPh$_3$)(η^1-'POH')] which NMR spectroscopy and X-ray crystallography showed to exist as mixtures of Ir–PPh$_2$C$_6$H$_4$N(Me)H-*o* and, respectively, Ir–PPh$_2$C$_6$H$_4$OH-*o* rotamers, stabilized by intramolecular N(Me)H···ClIr, OH···ClIr, or OH···H(Cl)Ir interactions,[1b,c] neither of the two isomeric forms of complex **2** features such intramolecular hydrogen bonding.

Since metal-to-ligand bonds other than Ir–H that could act as the weak base components toward the N–H bond as the weak acid components are absent in **2a** and **2b**, conceivable contributions to the preference for such sterically locked isomers could only arise from the involvement of the dangling methylamino substituent in hydrogen bonding to the *cis*-located Ir–H bond. Such interactions can be probed easily by the use of ^{1}H NMR NOE and variable temperature T_1 measurements.[10,11] For a nuclear Overhauser effect between any two dipole–dipole-coupled nuclei to be detectable, the two nuclei need to be <≈3 Å apart. This appears to be the case for molecules **2a**, where irradiation at the hydride resonance at δ −9.11 resulted in a 7% NOE enhancement for the NH peak at δ 5.42, as opposed to **2b**, where no measurable enhancement was observed for the NH region on selective irradiation of the hydride triplet at δ −9.48; yet isomer **2a** cannot be assigned a structure that differs from **2b** by tight N(Me)H···HIr hydrogen bonding as measurements of the spin–lattice relaxation times, T_1, made at 400 MHz as a function of temperature (Fig. 1) resulted in minimum T_1 values, $T_1^{(\min)}$, for the respective hydride ligands of 537 ms at 266 K for **2a** and of 513 ms at 277 K for **2b**. These are only slightly lower than the $T_1^{(\min)}$ of 588 ms measured at 255 K for complex **1**, which lacks any acidic E$^{\delta-}$–H$^{\delta+}$ bond that could behave as the proton donor toward Ir–H. Moreover, $T_1^{(\min)}$ values as low as ≈270 ms (at 400 MHz), in addition to NOE enhancements of more than 10%, have previously been measured for iridium complexes featuring unequivocal IrH···HN bonding,[4b,c] which clearly rules out the possibility of short H$^{\delta+}$···H$^{\delta-}$ contacts in **2a**.

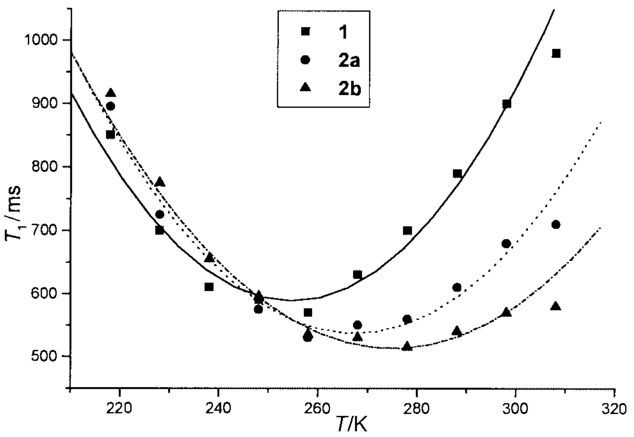


Fig. 1 Temperature dependence of the spin–lattice relaxation times, T_1, of **1**, **2a**, and **2b** at 400 MHz.

Hence, the ^{1}H and ^{31}P NMR spectral data observed for the two isomeric forms of **2** (see above) are most easily accommodated if the isomers are assigned structures in which the Ir–H bond is always *cis* to two near-equivalent *trans*-located phosphane ligands but can have either CO or C$_2$Ph as the *trans* ligand. The ^{13}C NMR spectra of the product mixtures containing **1** and **2a**/**2b** at 7 : 3 molar ratios are consistent with this view as the Ir–C$^\alpha$≡C$^\beta$Ph region[2] exhibits a triplet split by 3.7 Hz at δ 109.18 (**1**) together with three weaker singlets at δ 109.55, 110.22, and 110.37, which are attributed to the equivalent or non-equivalent carbon atoms C$^\beta$ of the *trans*- and *cis*-(PhC$_2$)$_2$Ir forms **2a** and **2b**, respectively. The carbon atom σ-bonded to the central metal of **1** gives rise to a well resolved triplet at δ 81.13 (*cis*-^2J(PC) = 12.6 Hz); a less intense and less resolved triplet (*cis*-^2J(PC) ≈ 12 Hz), assignable to the predominant isomer **a** of complex **2**, is seen at δ 82.0. It is concluded that this resonance arises from the two equivalent carbon atoms C$^\alpha$ of the molecules with *trans*-(PhC$_2$)$_2$Ir geometry (**2a**), while the corresponding signals caused by the two non-equivalent nuclei C$^\alpha$ of the *cis*-(Ph$_2$C)$_2$Ir form (**2b**) remain unobserved due to the distribution of intensity over two multiplets and the low concentration in solution of that geometric isomer.

Reactions with dimethyl acetylenedicarboxylate (dmad)

Combination of [Ir(CO)(PPh$_3$)('PNMe')] with dmad in toluene solution at room temperature, followed by triturating the evaporated mixture with methanol resulted in the isolation of [Ir{$C_2(CO_2Me)_2$}(CO)(PPh_3)(‘PNMe’)] **3** as the expected[12] 1 : 1 adduct, which is assigned an irida(III) cyclopropene structure with the ring carbon atoms *trans* to two mutually *cis*-coordinated phosphane ligands on the basis of IR and NMR (^{31}P, ^{13}C) evidence. The behaviour of the alkyne as an oxidatively added “doubly σ-bonded” chelate ligand manifests itself in a lowering of the $\nu(C\equiv C)$ wavenumber by ≈460 cm^{-1} from 2248 cm^{-1} in free dmad to 1784 cm^{-1} in **3**. The alkyne ^{13}C nuclei resonate at δ 93.60 and 96.93 as doublets of doublets with coupling constants $^2J(PC)$ of >60 Hz and <10 Hz, respectively, and thus clearly identify the coordination of the ring carbon atoms as *trans* with respect to two *cis*-bonded P donors. The small value of 33.3 Hz observed for $^2J(PP)$ is a further unequivocal indication of the mutual *cis* orientation of the PPh_3 and ‘PNMe’ ligands.

The analogous reaction between dmad and the rhodium(I) complex [Rh(CO)(PPh_3)(‘PNMe’)] resulted in insertion of the acetylene into the Rh–N bond rather than oxidative addition, forming the seven-membered metallaheterocycle [Rh{$C(CO_2Me)=C(CO_2Me)N(Me)C_6H_4PPh_2$-2}(CO)($PPh_3$)] **4**. The structure assigned to **4** was easily deduced from (a) the ^{31}P-{^1H} spectrum, indicating *trans*-positioned phosphane ligands [$^2J(PP)$ 304.1 Hz], and (b) the ^{13}C-{^1H} NMR data which revealed one metal-bonded ring carbon atom at δ 183.06 with strong coupling to ^{103}Rh [$^1J(RhC)$ 30.0 Hz] and two non-equivalent ^{31}P nuclei [*cis*-$^2J(PC)$ 18.9 and 11.7 Hz], accompanied by a non-coordinated vinylic carbon atom at δ 156.60 (d, $J = 10.7$ Hz) and a decoordinated methylamino function at δ 38.08 (s).

The formation of the insertion product **4**, where the central rhodium atom retains the +I oxidation state, as opposed to the irida(III)cyclopropene derivative **3**, can be looked on as a further example underscoring the decreased stability of the higher oxidation states for the 4d than for the 5d metals, so that in reactions of Rh^I and Ir^I complexes which may or may not result in oxidative addition, the Rh^{III} species are generally less prone to form than the corresponding Ir^{III} products.

While no reaction whatsoever occurred on combining [Rh(CO)(PPh_3)(‘PNH’)] with dmad in toluene, the homologous iridium(I) complex was observed to sluggishly interact with the alkyne, giving a 1 : 1 adduct together with quantities of unchanged starting materials. The adduct was readily identified as the metallacyclopropene complex [Ir{$C_2(CO_2Me)_2$}(CO)(PPh_3)(‘PNH’)] **5** on the basis of its spectral features which were perfectly in line with those found for complex **3**. In particular, the triple-bond stretching frequencies of both compounds were observed to be lowered by ≈460 cm^{-1} as compared to the free alkyne, and the resonances of the ring ^{13}C nuclei in **5** at δ 91.33 and 95.38 showed similar *trans*- and *cis*-coupling [$^2J(PC)$ >70 Hz and ≈10 Hz, respectively] to two non-equivalent *cis*-bonded phosphanes [$^2J(PP) \approx 36$ Hz] as those in **3**.

Attempts to separate metallacycle **5** from unreacted [Ir(CO)(PPh_3)(‘PNH’)] and free dmad resulted in an unexpected transformation as trituration of the crude solid with methanol [*i.e.*, the procedure that was successfully employed in the purification of **3** (see above)] furnished a yellow solid, displaying neither carbonyl nor alkyne stretching bands in the infrared. Moreover, the proton NMR of this material revealed the presence of three rather than two inequivalent methoxy groups, suggesting that the methanol solvent had reacted with the mixture. Since the exact nature of the product so generated could not be elucidated in a straightforward manner by means of vibrational and NMR spectroscopy, an X-ray diffraction study was undertaken.

The structure analysis revealed that treating the [Ir(CO)(PPh_3)(‘PNH’)]/[Ir{$C_2(CO_2Me)_2$}(CO)(PPh_3)(‘PNH’)] mixture with methanol had resulted in conversion into the iridium(III) complex [Ir{C(O)OMe}{$C(CO_2Me)=CH[C(O)OMe]$}(PPh_3)(‘PNH’)] **6**, whose central metal bears a chelating vinyl ligand which is coordinated through its α-carbon and a carbonyl oxygen atom of an ester substituent, in addition to an anionic methoxy(carbonyl) group and two unchanged PPh_3 and ‘PNH’ ligands (Fig. 2). The bonding within the metallacycle, where the CO_2Me groups adopt a *trans* configuration with respect to the C=C double bond can be considered to lie between two canonical structures, **A** and **B**, as previously proposed for a number of related vinyl metal complexes derived from dialkyl acetylenedicarboxylates.[13–17] For compound **6**, both structural and spectroscopic data indicate a significant contribution to the electronic description of the molecule by the carbene-like resonance structure **B** which tends to make the two carbon–carbon bond lengths within the ring more similar, to shorten the Ir–C^α bond, and to shift the resonance of the α-vinylic ^{13}C nucleus to lower field. Thus, the Ir–C(5) distance, 2.032(6) Å, is short for an iridium-to-carbon σ single bond, typically ranging from 2.13 to 2.20 Å in hexa-coordinate iridium(III) complexes.[18,19] The carbon–carbon bond lengths C(3)–C(4), 1.433(9) Å, and C(4)–C(5), 1.342(8) Å, differ by only 0.09 Å and thus compare favorably to, *e.g.*, the corresponding interatomic distances of 1.44(2) and 1.32(2) Å measured for the structurally related vinyl tungsten complex [W{$C(CO_2Bu^t)=CH(CO_2Bu^t)$}(CO)(NO)(PMe_3)], featuring significant carbenoid character,[14] but are in sharp contrast to [Ru{$C(CO_2Me)=CH(CO_2Me)$}$(CO)_2(PMe_2Ph)_2$]$^+$, where carbon–carbon bond lengths of 1.49(3) and 1.31(2) Å point to the presence of localized C–C single and double bonds within the five-membered chelate ring.[15] The ^{13}C resonance of the metal-bonded carbon atom, δ 193.84, is close to the chemical shift

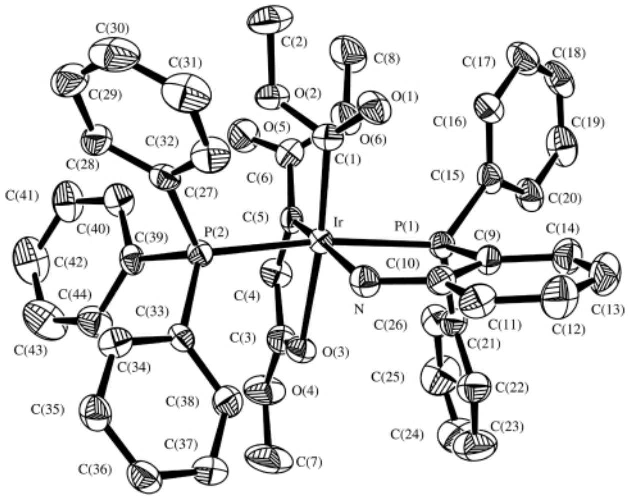
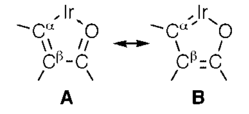


Fig. 2 Molecular structure of [Ir{C(O)OMe}{$C(CO_2Me)=CH-[C(O)OMe]$}(PPh_3)(‘PNH’)] **6**. Selected bond lengths (Å) and angles (°) with e.s.d.s: Ir–P(1) 2.3223(18), Ir–P(2) 2.3498(17), Ir–O(3) 2.262(4), Ir–N 2.105(5), Ir–C(1) 1.985(6), Ir–C(5) 2.032(6), C(1)–O(1) 1.210(7), C(1)–O(2) 1.367(7), C(3)–O(3) 1.253(8), C(3)–O(4) 1.328(8), C(6)–O(5) 1.199(8), C(6)–O(6) 1.314(8), C(3)–C(4) 1.433(9), C(4)–C(5) 1.342(8) and C(5)–C(6) 1.494(9); P(1)–Ir–P(2) 168.38(6), P(1)–Ir–O(3) 92.7(1), P(1)–Ir–N 79.4(1), P(1)–Ir–C(1) 91.9(2), P(1)–Ir–C(5) 94.1(2), P(2)–Ir–O(3) 84.5(1), P(2)–Ir–N 89.6(1), P(2)–Ir–C(1) 92.2(2), P(2)–Ir–C(5) 96.2(2), O(3)–Ir–N 95.2(2), O(3)–Ir–C(1) 172.5(2), O(3)–Ir–C(5) 77.1(2), N–Ir–C(1) 91.6(2), N–Ir–C(5) 169.8(2), C(1)–Ir–C(5) 96.6(3), Ir–C(1)–O(1) 128.1(5), Ir–C(1)–O(2) 112.2(5), Ir–O(3)–C(3) 108.7(4), Ir–C(5)–C(4) 116.6(5), Ir–C(5)–C(6) 128.8(5), O(1)–C(1)–O(2) 119.6(6), O(3)–C(3)–O(4) 121.8(7), O(5)–C(6)–O(6) 124.2(7), O(3)–C(3)–C(4) 122.0(6), O(4)–C(3)–C(4) 116.1(7), O(5)–C(6)–C(5) 124.2(7), O(6)–C(6)–C(5) 111.7(6), C(3)–C(4)–C(5) 115.6(6) and C(4)–C(5)–C(6) 114.7(6).



of δ 200.1 reported for the CH_2 group of $[Ir(=CH_2)\{N(SiMe_2CH_2PPh_2)_2\}]$[20] and thus supports the formulation of **6** as a "keto-vinyl↔enolato-carbene" resonance hybride; all the more as the latter iridium complex has a carbene carbon *trans*-bonded to an amido function, which is a structural feature of **6** as well. The Ir–C(O)OMe bond Ir–C(1), 1.985(6) Å, is rather short by comparison to the related distances of 2.05(2) and 2.073(8) Å found in $[IrI_2\{C(O)OMe\}(CO)(bipy)]$[21] and $[IrCl\{C(O)OMe\}(dmpe)_2]O_3SF$[22] and presumably reflects the weak *trans* influence of the ester oxygen atom *trans* to C(1).

The formation of **6** can be accounted for by postulating a reaction sequence that involves rapid insertion of $MeO_2CC{\equiv}CCO_2Me$ into a preformed Ir–H bond as a key-step. The ease of alkyne insertion into the metal–hydride function to give M–H/–C≡C– addition products with *cis* or *trans* stereochemistry has been demonstrated in numerous cases and, in fact, represents a general route to metal–vinyl complexes.[14,16,23] Although an iridium hydride could not be detected on combining $[Ir(CO)(PPh_3)$(‘PNH’)] with methanol,[24] we propose that the iridium(I) complex and MeOH can react to form such a species, *e.g.*, $[Ir(H)(OMe)(CO)(PPh_3)$(‘PNH’)], in an equilibrium that, at room temperature, lies very far to the Ir^I side. This view is consistent with the finding that complexes of the type $[Ir(H)(X)(OMe)(CO)(PR_3)_2]$ (formed from $[Ir(OMe)(CO)(PR_3)_2]$ by oxidative addition of HX; X = halide) are actually observable at low temperature but are unstable with respect to reductive elimination of methanol at 20 °C.[25] The σ-vinyl intermediate $[Ir\{C(CO_2Me)=CH(CO_2Me)\}(OMe)(CO)(PPh_3)$(‘PNH’)], resulting from dmad insertion into the Ir–H bond of the postulated hydride species, could undergo further transformation by adding the ketonic oxygen atom of one of its ester groups to the central metal to form the five-membered metallacyclic ring and induce cleavage of the Ir–OMe bond.[26] Subsequent nucleophilic attack by the methoxide ion on the proposed cationic carbonyl $[Ir\{C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)$(‘PNH’)]$^+$, which has ample literature precedence,[26,27] would then give **6** as the final product. The quantitative conversion by methanol of both constituents of the $[Ir(CO)(PPh_3)$(‘PNH’)]/$[Ir\{C_2(CO_2Me)_2\}(CO)(PPh_3)$(‘PNH’)] mixture into **6** is tentatively explained by postulating partial dissociation of the irida(III)cyclopropene complex **5** into $[Ir(CO)(PPh_3)$(‘PNH’)] and free dmad. Owing to the presence of a coordinated amido function NH^- in **5** which makes the central metal less electron-rich than the the *N*-methyl amido group NMe^- in $[Ir\{C_2(CO_2Me)_2\}(CO)(PPh_3)$(‘PNMe’)] **3**, metallacycle **5** is expected to have a higher propensity for reductive elimination than its homologue **3**, since influences that arise from the ligands and tend to decrease the electron density at the central metal make for an increase in reducibility of the molecule.

Experimental

General procedures

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents employed were distilled from the appropriate drying agents prior to use. IR spectra (in KBr): Mattson Polaris. NMR spectra: Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P) at 20 ± 2 °C with $SiMe_4$ as internal or with H_3PO_4 as external standard (downfield positive). Variable temperature T_1 measurements were made at 400.1 MHz (Bruker DRX 400) using the inversion recovery method. X-Ray structure analysis: Enraf-Nonius CAD 4 ($\lambda = 0.71073$ Å, $T = 293 \pm 2$ K); programs used for solution and refinement: SIR-97,[28] SHELXL-97.[29]

Preparations

$[IrH(C{\equiv}CPh)(CO)(PPh_3)$(‘PNMe’)] 1 and $[IrH(C{\equiv}CPh)_2(CO)(PPh_3)(\eta^1$-‘PN(Me)H’)] 2 (as *trans*- and *cis*-$(PhC_2)_2Ir$ isomers 2a and 2b). A solution of 150 mg (0.19 mmol) of $[Ir(CO)(PPh_3)$(‘PNMe’)][1b] in 15 mL of toluene was treated with 100 µL (1.05 mmol) of phenylacetylene and subsequently stirred at 70 °C for 3 h. The cooled mixture was carefully layered with pentane and allowed to stand at 5 °C for 3 d, which caused the precipitation of the products as an inseparable mixture of beige microcrystals [91 mg; product distribution (estimated by ^{31}P NMR): **1**: 70%; **2a**: 24%, **2b**: 6%]. $\tilde{\nu}_{max}/cm^{-1}$ ≈1970w (sh), ≈1985m (sh), 2001vs and 2118vs (C≡O,C≡C and IrH); $\delta_H(CDCl_3)$ −9.48 [1 H, t, *cis*-^2J(PH) 16.8 Hz, IrH of **2b**], −9.11 [1 H, t, *cis*-^2J(PH) 15.6 Hz, IrH of **2a**], −8.88 [1 H, t, *cis*-^2J(PH) 14.8 Hz, IrH of **1**], 2.23 [3 H, d, ^3J(HH) 4.9 Hz, NCH_3 of **2b**], 2.26 (3 H, s, NCH_3 of **1**), 2.55 [3 H, d, ^3J(HH) 4.8 Hz, NCH_3 of **2a**], 5.09 [1 H, q (br), NH of **2b**], 5.42 [1 H, q (br), NH of **2a**] and 6.2 to 7.7 (several m, C_6H_4 and C_6H_5); $\delta_C(CDCl_3)$ 21.46 (s, NCH_3 of **2a**), 29.89 (s, NCH_3 of **2b**), 30.35 (s, NCH_3 of **1**), 81.13 [t, *cis*-^2J(PC) 12.6 Hz, Ir*C*≡CPh of **1**], 82.0 [t, *cis*-^2J(PC) ≈12 Hz, Ir*C*≡CPh of **2a**], 109.18 [t, *J*(PC) 3.7 Hz, IrC≡*C*Ph of **1**], 109.55, 110.22 and 110.37 [all s (br), IrC≡*C*Ph of **2a** and **2b**] (C_6H_4 and C_6H_5 resonances omitted; IrCO and Ir*C*≡CPh of **2b** not assigned; see main text); $\delta_P(CDCl_3)$ −7.21 [1 P, A*B*-d, *trans*-^2J(PP) 333.2 Hz, **1** (assignment to PPh_3 or ‘PNMe’ uncertain)], −6.39 [2 P, apparent A_2 singlet, *i.e.*, $\Delta\nu \ll$ *trans*-^2J(PP), **2b**], 2.64 (2 P, apparent A_2 singlet, **2a**) and 3.03 [1 P, *A*B-d, PPh_3 or ‘PNMe’ of **1**].

$[Ir\{C_2(CO_2Me)_2\}(CO)(PPh_3)$(‘PNMe’)] 3. To a solution of 210 mg (0.27 mmol) of $[Ir(CO)(PPh_3)$(‘PNMe’)] in 15 mL of toluene 50 µL (0.41 mmol) of dmad was added *via* syringe. After stirring for 1 h at ambient conditions, solvent was removed *in vacuo* to leave the product as a yellow solid which was purified by washing with 15 mL of methanol (215 mg, 87%) [Found: C, 57.62; H, 4.19; N, 1.33. Calc. for $C_{44}H_{38}IrNO_5P_2$ (914.94): C, 57.76; H, 4.19; N, 1.53%]. $\tilde{\nu}_{max}/cm^{-1}$ 1694s (C=O), 1784s (C≡C) and 2003vs (C≡O); $\delta_H(C_6D_6)$ 2.76 (3 H, s, NCH_3), 3.09 (3 H, s, OCH_3), 3.74 (3 H, s, OCH_3), 6.6 (2 H, m), 6.9 (2 H, m), 7.0 (1 H, m), 7.2 (12 H, m), 7.3 (4 H, m), 7.5 (6 H, m) and 8.3 (2 H, m) (all C_6H_4 and C_6H_5); $\delta_C(C_6D_6)$ 41.01 (1 C, s, NCH_3), 51.43 (1 C, s, OCH_3), 52.22 (1 C, s, OCH_3), 93.60 [1 C, dd, *trans*-^2J(PC) 69.1 Hz, *cis*-^2J(PC) 9.0 Hz], 96.93 [1 C, dd, *trans*-^2J(PC) 65.0 Hz, *cis*-^2J(PC) 6.0 Hz] (both C≡C), 162.73 [1 C, t, *cis*-^2J(PC) 8.3 Hz, IrCO], 163.80 [1 C, dd, ^3J(PC) 10.1 and 7.6 Hz, C=O], 168.73 [1 C, d, ^2J(PC) 26.0 Hz, $C_{aryl}N$] and 171.04 [1 C, dd, ^3J(PC) 8.0 and 5.2 Hz, C=O] (C_6H_5 resonances and C_6H_4 signals other than $C_{aryl}N$ omitted; arbitrary assignments of IrCO and C=O, respectively); $\delta_P(C_6D_6)$ 9.99 [1 P, A*B*-d, *cis*-^2J(PP) 33.3 Hz, PPh_3] and 35.82 (1 P, *A*B-d, ‘PNMe’).

$[Rh\{C(CO_2Me)=C(CO_2Me)N(Me)C_6H_4PPh_2\text{-}2\}(CO)(PPh_3)]$ 4. The preparation was carried out as described for **3** by treating 260 mg (0.38 mmol) of $[Rh(CO)(PPh_3)$(‘PNMe’)][1b] with 47 µL (0.38 mmol) of dmad in 20 mL of toluene at room temperature for 9 h. Yield: 225 mg (72%) of **4** as yellow microcrystals [Found: C, 64.01; H, 4.62; N, 1.52. Calc. for $C_{44}H_{38}NO_5P_2Rh$ (825.65): C, 64.01; H, 4.64; N, 1.70%]. $\tilde{\nu}_{max}/cm^{-1}$ 1698s (C=O) and 1974 (C≡O); $\delta_H(C_6D_6)$ 2.74 (3 H, s, NCH_3), 2.92 (3 H, s, OCH_3), 3.29 (3 H, s, OCH_3), 6.7 (2 H, m), 7.2 (17 H, m) and 7.9 (10 H, m) (all C_6H_4 and C_6H_5); $\delta_C(C_6D_6)$ 38.08 (1 C, s, NCH_3), 50.07 (1 C, s, OCH_3), 50.64 (1 C, s, OCH_3), 156.60 (1 C, d, *J* 10.7 Hz, RhC=*C*N), 162.69 (1 C, d, *J* 1.9 Hz, C=O), 170.77 [1 C, dd, ^2J(PC) 30.6 Hz, ^3J(RhC) 2.7 Hz, $C_{aryl}N$], 172.10 (1 C, d, *J* 2.6 Hz, C=O), 183.06 [1 C, ddd, ^1J(RhC) 30.0, *cis*-^2J(PC) 18.9 and 11.7 Hz, Rh*C*=CN] and 195.41 [1 C, ddd, ^1J(RhC) 60.1, *cis*-^2J(PC) 15.4 and 12.3 Hz, RhCO] (C_6H_5 resonances and C_6H_4 signals other than $C_{aryl}N$ omitted); $\delta_P(C_6D_6)$ 34.04 [1 P, dd, ^1J(RhP) 145.4 Hz, *trans*-^2J(PP) 304.1 Hz, PPh_3] and 47.37 [1 P, dd, ^1J(RhP) 141.1 Hz, ‘PNMe’).

$[Ir\{C(O)OMe\}\{C(CO_2Me)=CH[C(O)OMe]\}(PPh_3)$(‘PNH’)] 6. The mixture of 200 mg (0.26 mmol) of $[Ir(CO)(PPh_3)$(‘PNH’)][1b] and 33 µL (0.26 mmol) of dmad in 15 mL of toluene was stirred for 2 h at room temperature. Evaporation of all volatile material left an oily residue consisting of unreacted starting materials, together with the metallacyclopropene complex $[Ir\{C_2(CO_2Me)_2\}(CO)(PPh_3)$(‘PNH’)] **5**: $\tilde{\nu}_{max}/cm^{-1}$ 1697s (C=O), 1788s (C≡C) and 2002vs (C≡O); $\delta_C(C_6D_6)$ 51.40 (1 C, s, OCH_3), 51.72 (1 C, s, OCH_3), 91.33 [1 C, dd, *trans*-^2J(PC) 74.5 Hz, *cis*-^2J(PC) 11.9 Hz], 95.38 [1 C, dd, *trans*-^2J(PC) 92.7 Hz, *cis*-^2J(PC) 8.9 Hz] (both C≡C), 162.42 [1 C, t, *cis*-^2J(PC) 11.0 Hz, IrCO], 163.67 (1 C, virtual t, $|^3J(PC) + {}^3J(P'C)|$ 22.1 Hz, C=O) and 171.91 (1 C, virtual. t, $|^3J(PC) + {}^3J(P'C)|$ 16.1 Hz, C=O) (C_6H_5 and C_6H_4 signals not assigned; arbitrary assignments of IrCO and C=O, respectively); $\delta_P(C_6D_6)$ 10.83 [1 P, A*B*-d, *cis*-^2J(PP) 35.8 Hz, PPh_3] and 39.02 (1 P, *A*B-d, ‘PNH’). The mixture was then dissolved in 20 mL of methanol. Partial evaporation of solvent caused complex **6** to separate from solution as orange crystals which were recystallized from toluene/pentane (195 mg, 80%) [Found: C, 56.45; H, 4.31; N, 1.31. Calc. for $C_{44}H_{40}IrNO_6P_2$ (932.91): C, 56.65; H, 4.32; N, 1.50%]. $\tilde{\nu}_{max}/cm^{-1}$ 1582vs, 1642vs, 1709vs (all C=O) and 3227w (NH); $\delta_H(C_6D_6)$ 2.93 (3 H, s), 3.27 (3 H, s), 3.52 (3 H, s) (all OCH_3), 4.73 [1 H, s (br), NH], 6.56 (1 H, dt, *J* 7.2 and 1.6 Hz, C_6H_4), 6.85 [1 H, s (br), =CH (?)], 6.9 (1 H, m), 7.1 (3 H, m), 7.3 (13 H, m), 7.40 [1 H, s (br)], 8.0 (8 H, m) and 8.4 (2 H, m) (all C_6H_4 and C_6H_5); $\delta_C(C_6D_6)$ 50.43 (1 C, s), 50.95 (1 C, s), 52.22 (1 C, s) (all OCH_3), 122.78 (1 C, s, IrC=*C*H), 146.20 [1 C, t, *cis*-^2J(PC) 7.6 Hz, Ir*C*O$_2$Me], 170.71 [1 C, dd, *J*(PC) 23.3 and 5.7 Hz, $C_{aryl}N$], 178.32 (1 C, s), 182.94 (1 C, s) (both C*C*O$_2$Me) and 193.84 [1 C, t, *cis*-^2J(PC) 6.6 Hz, Ir*C*=CH] (C_6H_5 resonances and C_6H_4 signals other than $C_{aryl}N$ omitted); $\delta_P(C_6D_6)$ 24.16 [1 P, A*B*-d, *trans*-^2J(PP) 332.7 Hz, PPh_3] and 38.62 (1 P, *A*B-d, ‘PNH’).

Crystal and refinement data for complex 6

$C_{44}H_{40}IrNO_6P_2$, $M = 932.91$, monoclinic, space group $P2_1/n$, $a = 13.320(1)$, $b = 18.325(9)$, $c = 16.197(1)$ Å, $\beta = 98.093(7)°$, $U = 3914(2)$ Å^3, $Z = 4$, $D_c = 1.583$ Mg m^{-3}, μ(Mo-Kα) = 3.543 mm^{-1}; 8169 reflections collected, 6873 reflections unique ($R_{int} = 0.0378$) which were used in all calculations; $R_w{}^2 = 0.0734$ for all data, 490 parameters, and 0 restraints, $R = 0.0422$ for 4605 data with $I > 2\sigma(I)$.

CCDC reference number 186/1677.

See http://www.rsc.org/suppdata/dt/1999/3935/ for crystallographic files in .cif format.

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