Synthesis of η^4:π^2-Exocyclic-Diene Iridium(I) Complexes Derived from 1,3-Oxazolidin-2-ones and Their Transformation into Iridium(III) Derivatives by Reaction with a Phosphine and with Aldehydes

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Received July 12, 2005

The reaction of the dimer $[Ir(\mu\text{-}Cl)(coe)_2]_2$ with two exocyclic dienes like N-substituted 4,5-dimethylene-2-oxazolidinones **a** and **b**, and KTp^{Me2} yields derivatives of the composition $Tp^{Me2}Ir$(**a** or **b**) (**1a**,**b**). Derivative **1a** reacts with $Ph_2PC{\equiv}CPPh_2$, with the formal oxidative addition of the diene moiety to the metal center and coordination of the phosphine in the κ^1 mode. Derivatives **1a**,**b** react with aromatic aldehydes to form the new compounds **3** (with benzaldehyde) and **4** (anisaldehyde), which contain an elaborated bidentate ligand formed by coupling of the two organic fragments (diene and aldehyde). The structures of compounds **3a**,**b** have been determined by X-ray diffraction analysis.

Introduction

Ir butadienes and their methyl derivatives of composition $Tp^{Me2}Ir(CH_2{=}C(R)C(R){=}CH_2)$ (R = H, Me; Tp^{Me2} = hydrotris-(3,5-dimethylpyrazolyl)borate[1]) have shown to exhibit a reactivity quite different from that of monomer olefin compounds in C−H activation processes.[2] The Ir(I) complexes $Tp^{Me2}Ir(CH_2{=}CHR)_2$ (R = H, Me) (which contain ethylene or propene) easily react thermally by C−H activation, either intramolecularly[3] or toward hard bases[4] or other hydrocarbons,[5] and experience olefin substitution when reacted with soft bases.[6] In contrast, compounds of the composition $Tp^{Me2}Ir(CH_2{=}C(R)C(R){=}CH_2)$[7] (R = H, Me) are very reluctant to experience intramolecular thermal C−H activation, which requires photochemical irradiation to take place. These compounds react with either soft or hard Lewis bases to yield Ir(III) adducts in which the diene has experienced a formal oxidative addition process to the metal center.[8] This process is on occasion followed by subsequent steps, including C−C or C−X bond formation involving the diene moiety and the Lewis base.[9] For aldehydes, this reaction ultimately yields products resulting from the formal decarbonylation of this substrate, but the reaction has been shown to proceed through a series of isolable kinetic intermediates with a bicyclic structure.[10] In this contribution we report the preparation of novel diene Ir complexes derived from the N-substituted exocyclic dienes 4,5-dimethylene-2-oxazolidinone (**a**, **b**). These dienes[11] have proved to be highly reactive, both regio- and stereoselectively, in Diels−Alder cycloadditions.[12] The observed reactivity and selectivity were mainly due to the strong activation of the diene moiety by the heteroatoms of the heterocyclic ring. Among these heteroatoms, the nitrogen atom displayed the strongest electron-donor effect, controlling the regioselectivity in Diels−Alder reactions, and in the oxidative cleavage by treatment of the diene with *m*-chloroperbenzoic acid.[13] In addition, we have

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(1) (a) Trofimenko, S. *Scorpionates-The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (d) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (e) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *Adv. Organomet. Chem.* **1992**, *34*, 1. (f) Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.

(2) (a) Nikonov, G. I.; Mountford, P.; Ignatov, S. K.; Green, J. C.; Leech, M. A.; Kuzmina, L. G.; Razuvaev, A. G.; Rees, N. H.; Blake, A. J.; Howard, J. A. K.; Lemenovskii, D. A. *Dalton Trans.* **2001**, 2903. (b) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. (c) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1699. (d) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen. A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953. (e) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (f) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(3) Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.

(4) Alías, F. M.; Daff, P. J.; Paneque, M.; Poveda, M. L.; Carmona, E.; Pérez, P. J.; Salazar, V.; Alvarado, Y.; Atencio, R.; Sánchez-Delgado, R. *Chem. Eur. J.* **2002**, *8*, 5132.

(5) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem. Eur. J.* **1998**, *4*, 2225.

(6) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.

(7) Boutry, O.; Poveda, M. L.; Carmona, E. *J. Organomet. Chem.* **1997**, *528*, 143.

(8) Paneque, M.; Poveda, M. L.; Salazar, V.; Gutiérrez-Puebla, E.; Monge, A. *Organometallics* **2000**, *19*, 3120.

(9) Paneque, M.; Poveda, M. L.; Salazar, V.; Taboada, S.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Ruiz, C. *Organometallics* **1999**, *18*, 139.

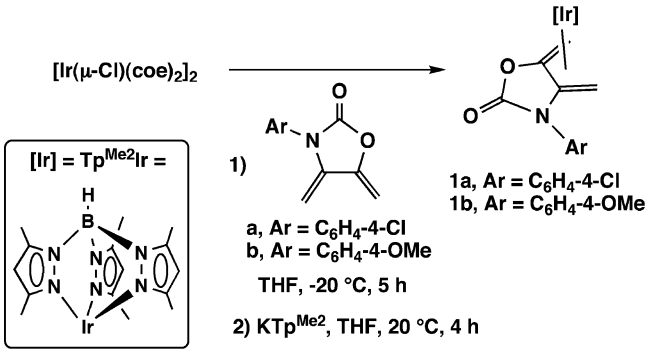
(10) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248.

(11) Hernandez, R.; Sanchez, J. M.; Gomez, A.; Trujillo, G.; Aboytes, R.; Zepeda, G.; Bates, R. W.; Tamariz, J. *Heterocycles* **1993**, *36*, 1951.

(12) Mandal, A. B.; Gomez, A.; Trujillo, G.; Mendez, F.; Jimenez, H. A.; Rosales, M. J.; Martinez, R.; Delgado, F.; Tamariz, J. *J. Org. Chem.* **1997**, *62*, 4105.

10.1021/om050582z CCC: $33.50
Publication on Web 11/30/2005

Scheme 1



carried out the reaction of one of the Ir−diene complexes prepared, with a phosphine, to yield an Ir(III) adduct, and with aldehydes, to yield metallabicyclic compounds whose formation implies C−H activation, C−C bond formation, and decarboxylation of the original diene.

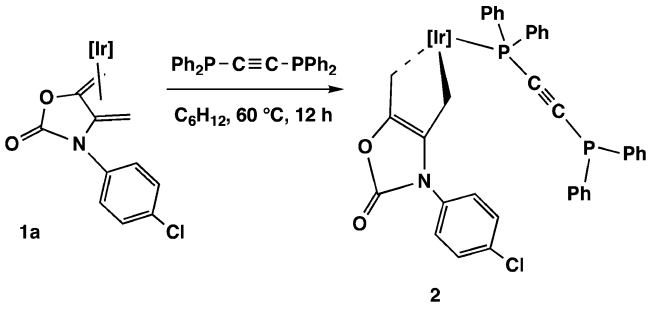
Results and Discussion

The reaction of the dimer $[Ir(\mu\text{-Cl})(coe)_2]_2$ with 2 equiv of the exocyclic dienes **a**,**b** followed by the addition of KTp^{Me2}, under the appropriate conditions, affords the corresponding $Tp^{Me2}Ir$(diene) complexes **1a**,**b** in good yields (Scheme 1).

Compounds **1** are quite stable in the solid state but slowly decompose in solution, with decoordination of the diene. Thus, a sample kept in C_6D_6 at room temperature showed, after 24 h, complete displacement of the diene, which was identified spectroscopically in the solution. The NMR data recorded revealed the presence in the sample of the known $Tp^{Me2}Ir(Ph)_2N_2$[5] (fully deuterated in the Ph rings), but this reaction was not studied in more detail.

Compounds **1** were fully characterized by spectroscopy and elemental analysis. For **1a**, the two nonequivalent and diastereotopic CH_2 groups generate four doublets, two of them overlapping at 3.3 ppm and the other two at 0.94 and 0.67 ppm, in the ^{1}H NMR spectrum. These signals are found at chemical shifts very close to those found for the parent butadiene and Me-substituted butadiene derivatives.[7] The corresponding terminal carbons $=CH_2$ for **1a** resonate at −11.3 and −11.8 ppm, at higher fields than the respective C atoms in the referenced parent complexes with no heteroatoms in the diene ligands (between 0 and 5 ppm), probably due to the presence in each adjacent carbon of electron-donor N and O functionalities. The $^1J_{CH}$ value for the terminal CH_2 groups amounts to 154 Hz. Assuming that the relationship between the C−H coupling constant and % s character of the carbon orbital is given by the equation[14] $J_{C-H} = 5.7(\%\ s) - 18.4$ Hz, we can calculate that these methylene carbon atoms have 30.24% of s character, and hence the nature of these moieties is mainly sp^2. Therefore, it can be concluded that these dienes coordinate to the Ir atom in the η^4:π^2 coordination mode,[15] with perhaps a very small contribution of the η^4:σ^2,π mode, widely found for the early transition metals.[16]

Scheme 2



To test the chemical behavior of these diene complexes toward Lewis bases, and compare it with that of the parent compounds, the reactivity of **1a** with a phosphine derivative, $Ph_2PC{\equiv}CPPh_2$ (1,2-bis(diphenylphosphino)ethyne) was carried out.[17] The reaction is complete after 12 h at 60 °C, to provide the new compound **2**, which is isolated in 50% yield after workup (Scheme 2).

The NMR data registered for compound **2** are in agreement with the structure depicted. κ^1 coordination of the phosphine is authenticated by the observation of two singlets in a 1:1 ratio in the $^{31}P\{^1H\}$ NMR spectrum, at δ 9.3 and −19.8 ppm, corresponding respectively to the Ir-coordinated and free ends (δ −31.2 ppm in the free ligand). Although a chemical shift could have been expected for the noncoordinated end that was identical, or almost identical, with that of the free molecule, this signal shifts ca. 12 ppm toward low field, and it could be proposed that transfer of electron density through the triple bond of the diphosphine ligand is responsible for this behavior. $^{13}C\{^1H\}$ NMR data show resonances at −9.7 and −13.7 ppm for the C atoms of the methylene moieties bound to Ir. The sp^3 nature of these atoms can be deduced from their values of $^1J_{CH}$, which amount to 130 Hz (average) (if the equation mentioned above is applied in this case, a % s character of 26% is deduced). In agreement with the cis disposition with respect to the phosphine ligand, they have small coupling constant values ($^2J_{CP}$ = 6.4 Hz in each case).[18] Coupling to the phosphine ligand is also responsible for the splitting of two of the ^{1}H NMR resonances corresponding to the methylene protons, with values analogous to those found for the related compounds $Tp^{Me2}Ir(CH_2C(R){=}C(R)CH_2)(PMe_3)$ (R = H, Me).[8]

It is worth mentioning that, in addition of the P atoms, two other potentially reactive sites are present in the phosphine ligand: the phenyl rings and the C−C triple bond. Despite the facility with which these types of $Tp^{Me2}Ir$ compounds react with aromatic molecules[5,9,18] (see also above), ortho metalation of the ligand is not observed. Also, the reaction of the compound $Tp^{Me2}Ir(CH_2{=}C(Me)C(Me){=}CH_2)$ with alkynes has been reported recently, which takes place by displacement of the diene ligand.[19] In this case, the preferred reaction is coordination of the P atom.

The feasibility of an analogous reactivity of these diene compounds **1** toward Lewis bases, in comparison with the

(13) (a) Martinez, R.; Jimenez-Vazquez, H. A.; Reyes, A.; Tamariz, J. *Helv. Chim. Acta* **2002**, *85*, 464. (b) Benavides, A.; Martínez, P.; Jiménez-Vázquez, H. A.; Delgado, F.; Tamariz, J. *Heterocycles* **2001**, *55*, 469.

(14) (a) Newton, M. D.; Schulman, J. M.; Manus, M. M. *J. Am. Chem. Soc.* **1981**, *103*, 17. (b) McMurry, J. E.; Lectka, T.; Hodge, C. N. *J. Am. Chem. Soc.* **1989**, *111*, 8867.

(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(16) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

(17) Although this is not a common phosphine, it was the only one available in our laboratory for this study.

(18) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

(19) Álvarez, E.; Gómez, M.; Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Rojas-Lima, S.; Salazar, V.; Mereiter, K.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1478.

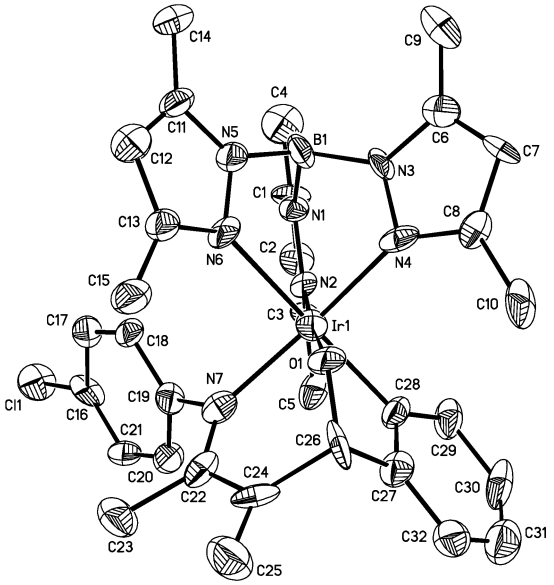
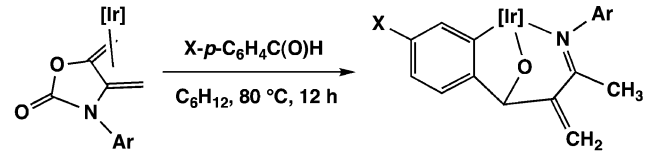


Figure 1. ORTEP representation of the molecular structure of compound **3a** (ellipsoids with 30% probability). Hydrogen atoms and the dichloromethane solvent molecule have been omitted for clarity.

Scheme 3



1a, Ar = C_6H_4-4-Cl
1b, Ar = C_6H_4-4-OMe

	Ar	X
3a	C_6H_4-*p*-Cl	H
4a	C_6H_4-*p*-Cl	OMe
3b	C_6H_4-*p*-OMe	H
4b	C_6H_4-*p*-OMe	OMe

simpler parent derivatives with unsubstituted or methylated butadiene, prompted us to investigate the reactivity of **1** with aldehydes, which have shown interesting reactivity toward the parent diene compounds.[10] Hence, we have reacted both **1a** and **1b** with an excess of benzaldehyde or anisaldehyde. In all cases the reaction proceed cleanly to yield derivatives **3** and **4**, isolated in moderate to low yields after column chromatography. These reactions require ca. 12 h at 60 °C to proceed to completion (^{1}H NMR monitoring), no intermediates being detected in the reaction mixtures besides the starting materials or the end products. They are structurally analogous in all cases studied, and hence, this process seems to be very general for these types of activated dienes and aromatic aldehydes.

As can be seen in Scheme 3, the transformation is very complex and involves not only coupling of the carbonyl carbon atom of the aldehyde with the original diene but also its decarboxylation and the ortho metalation of the aldehyde phenyl ring. In full, this reaction yields bicyclic derivatives with aryl, alkoxy,[20] and imine[21] ends. Despite the presence of an excess of aldehyde in the reaction mixture, only one molecule of this substrate is incorporated in the final product. By comparison with the reactivity observed for these systems toward Lewis bases, it can be proposed that the reaction starts by coordination of the aldehyde, forming an intermediate analogous to **2**, but we have not been able to gather more mechanistic information, due to the complexity of the process.

(20) (a) Cámpora, J.; Matas, I.; Palma, P.; Graiff, C.; Tiripicchio, A. *Organometallics* **2005**, *24*, 2827. (b) For other Tp^{Me2}Ir alkoxy compounds see ref 4.

(21) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275.

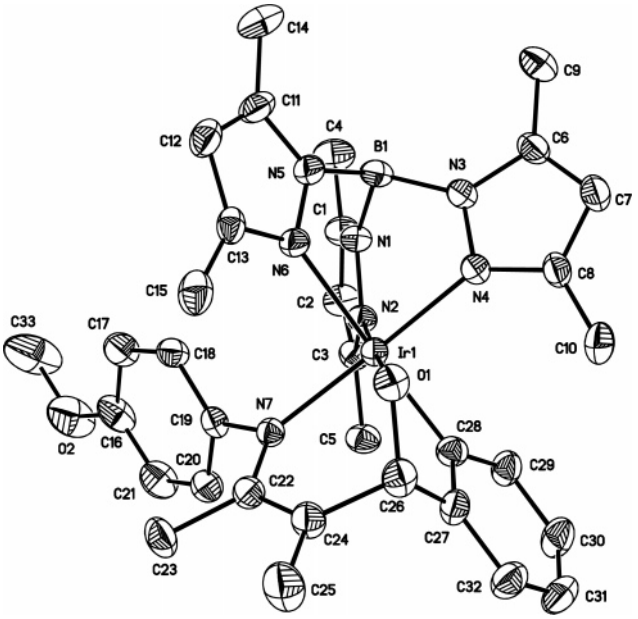


Figure 2. ORTEP representation of the molecular structure of compound **3b** (ellipsoids with 30% probability). Hydrogen atoms and the ethanol solvent molecule have been omitted for clarity.

Table 1. Crystal Data and Structure Refinement Details for Compounds 3a and 3b

	3a	3b
formula	$C_{33}H_{38}BCl_3IrN_7O$	$C_{35}H_{45}BIrN_7O_3$
mol wt	858.06	814.79
color	red	red
cryst size	0.19 × 0.16 × 0.07	0.57 × 0.40 × 0.32
sym, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	11.3259(12)	9.707(7)
b, Å	21.219(2)	26.84(3)
c, Å	15.0905(16)	14.283(7)
α, deg	90	90
β, deg	100.147(2)	107.93(2)
γ, deg	90	90
V, Å^3	3569.9(7)	3540(5)
Z	4	4
D_{calcd}, g cm^{-3}	1.57	1.53
diffractometer	Bruker SMART 5000 CCD	
λ(Mo Kα), Å	0.710 73	
monochromator	graphite	
scan type	*ω* scans	
μ, mm^{-1}	4.0	3.8
2*θ* range, deg	3.34−37.36	1.52−26.02
temp, K	293(2)	293(2)
no. of data collected	10 625	23 256
no. of unique data	2741 (R_{int} = 0.0894)	6940
no. of params/restraints	419/0	429/0
R1[a] ($F^2 > 2\sigma(F^2)$)	4.5	3.5
wR2[b] (all data)	11.1	7.8
S[c] (all data)	0.962	1.01

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

Unequivocal characterization of these species was performed by the X-ray structure analysis of two of these derivatives, namely **3a** and **3b**. Figures 1 and 2 show ORTEP representations of their molecules, while Tables 1 and 2 respectively contain crystal data and selected bond distances and angles. For the case of **3a** the structure can be described as a distorted octahedron, with a value for the angle O(1)−Ir(1)−C(28) (82.2-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 3a and 3b

	3a	3b
	Bond Distances	
Ir(1)−N(6)	2.184(14)	2.192(4)
Ir(1)−N(2)	2.022(16)	2.095(4)
Ir(1)−N(4)	2.039(12)	2.063(4)
Ir(1)−N(7)	2.068(14)	2.080(4)
Ir(1)−C(28)	2.057(15)	2.025(5)
Ir(1)−O(1)	1.972(12)	2.030(4)
C(26)−O(1)	1.33(2)	1.420(6)
C(24)−C(25)	1.33(2)	1.329(7)
C(22)−C(23)	1.57(2)	1.515(7)
	Bond Angles	
N(2)−Ir(1)−N(4)	85.5(6)	86.15(15)
N(2)−Ir(1)−N(6)	90.3(6)	90.25(15)
N(2)−Ir(1)−N(7)	97.0(6)	95.57(14)
N(4)−Ir(1)−N(6)	86.5(5)	86.44(15)
N(4)−Ir(1)−N(7)	175.5(5)	177.37(14)
N(4)−Ir(1)−C(28)	91.9(6)	91.68(19)
N(4)−Ir(1)−O(1)	89.6(5)	91.29(14)
O(1)−Ir(1)−C(28)	82.2(7)	82.18(16)
O(1)−Ir(1)−N(2)	175.0(5)	177.31(13)

(7)°) smaller than the ideal 90°, probably due to the small size of the metallacycle (five-membered). The other two angles involved in the bicyclic unit are close to the ideal value (O(1)−Ir(1)−N(7) = 87.8(6)°, N(7)−Ir(1)−C(28) = 91.4(6)°). The distances Ir−C(28) = 2.057(13) Å and Ir−O(1) = 1.972(12) Å agree with that for a single bond. With respect to the exocyclic bonds, C(24)−C(25) (1.33(2) Å) is a clearly double bond, while the C(22)−C(23) distance amounts to 1.57(2) Å, in agreement with its single-bond character. The distance Ir−N(6) (2.184(12) Å), trans to the aryl moiety of the N,O,C ligand, is greater than the other two (Ir−N(2) = 2.022(16) Å, Ir−N(4) = 2.039(14) Å), and reflects the higher trans influence of the aryl ligand as compared with that of the other two ends.

Analogous data have been obtained for derivative **3b**.

The NMR data recorded for these compounds are in agreement with the structure found in the solid state. Thus, taking **3a** as a representative example, in the ^{1}H NMR signals for four protons are found (7.24, 6.89 (2H), and 6.75 ppm) for the aromatic protons of the original benzaldehyde, which is ortho metalated in the final compound. The signals due to the four protons of the N−Ar ring are shown as doublets of doublets, at 6.97, 6.66, 6.53, and 5.97 ppm, as a consequence of their nonequivalent environments, owing to the coordination of the N atom to Ir. This proton nonequivalence suggests a restricted rotation around the N−Ar bond, at room temperature, probably due to the crowded environment of the ring in the close proximity of the Ir center, to which the N atom is bonded. The exocyclic methylene group resonates at 6.16 and 5.96 ppm. In the ^{13}C{^{1}H} NMR spectrum, the signal for the imine carbon atom, Ir−N=C, appears at 175.4 ppm. Finally, the vibration of the C=N bond is responsible for the IR band at 1725 cm^{-1}.

In conclusion, we have shown that substituted 1,3-oxazolidin-2-ones can bind to the Tp^{Me2}Ir fragment in mainly the η^4:π^2 fashion found previously for other Tp^{Me2}Ir(butadiene) compounds. These derivatives react with a phosphine to experience a change in the coordination mode of the diene moiety, to η^2:σ^2, as deduced by NMR, and with aromatic aldehydes, following a complex, undisclosed, pathway which ends with the elaboration of a bidentate ligand with aryl, alkoxy, and imine termini. This reaction involves coupling of the carbonyl carbon atom of the aldehyde with the diene, decarbonylation of that moiety, and ortho metalation of the aldehyde phenyl ring.

Experimental Section

General Procedures. All preparations and manipulations were carried out under nitrogen or argon following conventional Schlenk techniques. Solvents were dried rigorously and degassed before use. The compounds prepared were purified by flash column chromatography, through silica gel (Merck 60, 230−400 mesh). Microanalyses were recorded on a Perkin-Elmer Series II 2400 apparatus. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR instrument in KBr and NMR spectra on a JEOL Eclipse 400 spectrometer using $CDCl_3$ as the solvent. The ^{1}H and ^{13}C residual resonance signals of the solvent were used as internal standards, but chemical shifts are reported with respect to TMS. ^{31}P NMR shifts were referenced to external 85% H_3PO_4. Most of the NMR assignments are based on extensive ^{1}H−^{1}H decoupling experiments and homo- and heteronuclear two-dimensional spectra. Despite repeated efforts, we have been unable to obtain reliable elemental analysis data for most of the compounds reported. To show the purity of the samples, we have included in the Supporting Information a complete set of NMR spectra.

Synthesis of the Compound [Tp^{Me2}Ir(CH$_2$=C(N(4-ClC$_6$H$_4$)C(O)O)C=CH$_2$)] (1a). To a suspension of [Ir(μ-Cl)(coe)$_2$]$_2$ (0.104 g, 0.155 mmol) in THF (20 mL) cooled to −20 °C was added (4-chlorophenyl)-4,5-dimethylene-2-oxazolidinone (0.068 g, 0.306 mmol). The mixture was stirred for 20 min, during which time it turned brown. Inmediately afterward, a solution of KTp^{Me2} (0.080 g, 0.239 mmol) in THF (20 mL) was transferred and the mixture was stirred for 4 h at 20 °C. After this time, the solvent was removed under vacuum and the product extracted with a mixture of CH_2Cl_2 and Et_2O (20 mL, 50/50). The solid was eliminated by centrifugation and the resulting solution cooled to −20 °C, to yield compound **1a** as a brown powder (0.075 g, 68% yield). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.67, 7.43 (2d, 2H each, $^3J_{HH}$ = 8.8 Hz, 4CH$_{Ph}$), 5.81, 5.69, 5.54 (3s, 1H each, 3CHpz), 3.31, 3.29, 0.94, 0.67 (4d, 1H each $^2J_{HH}$ = 6.1, 6.5, 6.6, and 6.2 Hz, respectively, 2CH$_2$), 2.38, 2.31, 2.27, 2.19, 1.58 (6s, 1:2:1:1:1, 3H each, 6Me$_{pz}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 155.6 (CO), 153.7, 151.6, 149.5, 143.4, 143.2, 143.1 (Cq$_{pz}$), 134.8, 132.2 (Cq$_{Ph}$), 129.4, 124.3 ($^1J_{CH}$ = 166 Hz, 2 and 2CH$_{Ph}$), 107.8, 107.3, 106.7 ($^1J_{CH}$ = 172 Hz, CH$_{pz}$), 107.0, 98.0 (Cq$_{dien}$), 15.1, 14.4, 14.3, 13.0, 12.6 (1:1:1:2:1, $^1J_{CH}$ = 127 Hz, Me$_{pz}$), −11.3, −11.8 ($^1J_{CH}$ = 154 Hz, Ir−CH$_2$=). IR (KBr): ν 2529.0 (B−H), 1779.1 (CO) cm^{-1}. Anal. Calcd for $C_{26}H_{30}BClN_7O_2Ir\cdot CH_2Cl_2$ (mol wt 796): C, 40.74; H, 4.05; N, 12.32. Found: C, 41.0; H, 4.6; N, 11.8.

Synthesis of the Compound [Tp^{Me2}Ir(CH$_2$=C(N(4-CH$_3$-OC$_6$H$_4$)C(O)O)C=CH$_2$)] (1b). To a suspension of [Ir(μ-Cl)(coe)$_2$]$_2$ (0.10 g, 0.15 mmol) in THF (20 mL) cooled to −20 °C was added (4-methoxyphenyl)-4,5-dimethylen-1,3-oxazolidin-2-one (0.065 g, 0.31 mmol). After 20 min of stirring, the reaction mixture turned pale brown. A solution of KTp^{Me2} (0.078 g, 0.233 mmol, in 20 mL of THF) was then transferred into the reaction flask and the mixture stirred for 4 h at 20 °C. After this time, the solvent was removed under vacuum and the solid extracted with a mixture of CH_2Cl_2/Et_2O (20 mL, 50/50). After centrifugation to remove the solid residue, the solution was kept at −20 °C, to yield a pale brown powder (0.067 g, 63% yield). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.59 (d, 2H, $^3J_{HH}$ = 8.8 Hz, 2CH$_{Ph}$), 6.96 (d, 2H, $^3J_{HH}$ = 9.2 Hz, 2CH$_{Ph}$), 5.81, 5.69, 5.54 (3s, 1H each, 3CH$_{pz}$), 3.89 (s, 3H, OMe), 3.27, 3.26, 0.92, 0.64 (4d, 1H each, $^2J_{HH}$ = 6.2, 6.7, 6.6, 6.2 Hz, respectively, 2CH$_2$), 2.38, 2.32, 2.31, 2.27, 2.20, 1.61 (6s, 3H each, 6Me$_{pz}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 156.2 (CO), 153.8, 151.6, 149.6, 143.3, 143.1, 143.0 (Cq$_{pz}$), 158.1, 129.0 (Cq$_{Ph}$), 124.8, 114.4 (CH$_{Ph}$), 107.7, 107.3, 106.1 ($^1J_{CH}$ = 176.8 Hz, CH$_{pz}$), 106.0, 99.2 (Cq$_{dien}$), 55.6 (OMe), 15.1, 14.3, 12.9, 12.6 (1:2:2:1, Me$_{pz}$), −11.7, −12.0 ($^1J_{CH}$ = 154 Hz, 2 CH$_2$). IR (KBr): ν 2526.8 (B−H), 1778.6 (CO) cm^{-1}.

Synthesis of Compound 2. To a suspension of compound **1b** (0.05 g, 0.071 mmol) in cyclohexane (3 mL) was added (Ph)$_2$PC≡

$CP(Ph)_2$ (0.028 g, 0.071 mmol). The suspension was stirred for 12 h at 60 °C. After this time, the solvent was removed under vacuum and diethyl ether (10 mL) was added, the mixture being shaked for a few minutes. The solvent was removed and the residue recrystallized from ethyl acetate/hexane at −20 °C, giving 0.040 g of the title compound (51% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 9.3 (P−Ir), −19.8 (C−P). ^1H NMR ($CDCl_3$, 25 °C): δ 7.93−6.9 (m, 20H, P−Ph), 6.83, 7.35 (d, 2H each, $^3J_{HH}$ = 9.2 Hz, CH_{ArOMe}), 5.69, 5.50, 5.39 (3s, 1H each, CH_{pz}), 3.78 (s, 3H, OMe), 2.53 (br s, 2H, CH_2), 2.98, 2.77 (2dd, $^2J_{HH}$ = 14.5 Hz, $^3J_{HP}$ = 8.5 and 3.0 Hz, respectively, CH_2), 2.04 (d, 3H, J_{HP} = 1.1 Hz, Me_{pz}), 2.40, 2.37, 2.27, 1.46, 1.30 (6s, 3H each, $6Me_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 400 MHz): δ 171.3 (C═O), 159.4, 157.8 (Cq_{PhOMe}), 150.3, 136.5 (Ir−CH_2*C*═*C*), 152.5, 152.1, 150.6, 144.2, 143.8, 143.3 (Cq_{pz}), 132.0, 130.6, 129.1 (d, $^1J_{CP}$ = 62.7 Hz, $3Cq_{PPh}$), 128−134 ppm (overlapping doublets, CH_{PPh} and $1Cq_{PPh}$), 125.6, 114.4 (4 CH_{PhOMe}), 109.1, 108.4, 108.2 (CH_{pz}), 100.3 (dd, $^1J_{CP}$ = 70, $^2J_{CP}$ = 18 Hz, Ir−PC≡), 99.6 (d, $^1J_{PC}$ = 144 Hz, Ir−PC≡*C*), 55.6 (OCH_3), 14.5, 14.3, 13.2, 13.0, 12.9, 12.0 (CH_{3pz}), −9.7, −13.7 (d, $^2J_{CP}$ = 6.4, Ir−CH_2). IR (KBr): ν 2533, 1748, 827 cm^{-1}.

Synthesis of Compound 3a. To a suspension of **1a** (0.100 g, 0.140 mmol) in cyclohexane (3 mL) was added freshly distilled benzaldehyde (0.3 mL, 2.94 mmol). The suspension was stirred for 12 h at 60 °C. After this time, the solvent was removed under vacuum and diethyl ether (10 mL) was added, the mixture being stirred vigorously for a few minutes. After this period of time, the solvent was evaporated and a ^1H NMR spectrum of this solid residue ($CDCl_3$) showed almost quantitative formation of the title product. It was purified by column chromatography using silica gel. Recrystallization from Et_2O at −20 °C afforded the title compound as prismatic red crystals (0.06 g, 54% yield). ^1H NMR ($CDCl_3$, 25 °C): δ 7.24 (dd, 1H, J_{HH} = 7.7, 1.1 Hz), 6.89 (br m, 2H), 6.75 (dd, 1H, J_{HH} = 7.3, 1.1 Hz) (Ir−C_6H_4), 6.97 (dd, 1H, J_{HH} = 8.4, 2.2 Hz), 6.66 (dd, 1H, J_{HH} = 8.8, 2.6 Hz), 6.53 (dd, 1H, J_{HH} = 8.4, 2.6 Hz), 5.97 (dd, 1H, J_{HH} = 8.8, 2.5 Hz) (N−C_6H_4), 6.16 (s, 1H, ═CH_2), 5.96 (s, 1H, ═CH_2), 5.87, 5.43, 5.39 (s, 1H each, CH_{pz}), 5.24 (s, 1H, O−CH), 2.48, 2.43, 2.37, 2.29, 1.62, 1.33 (s, 3 H each, 6 Me_{pz}), 2.05 (s, 3 H, Me−C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 175.4 (C═N), 160.5 (Ir−C), 152.0, 151.8, 150.6, 143.9, 143.5, 142.7 (Cq_{pz}), 151.5 (C−N), 150.7 (*C*═CH_2), 141.2 (*C*−C(H)O), 138.9, 122.9, 122.6, 118.5 (CH, Ir−C_6H_4), 132.2 (C−Cl), 128.4, 128.3, 126.7, 124.2 (CH, N−C_6H_4), 121.8 (CH_2), 107.9, 107.6, 106.1 (CH_{pz}), 88.7 (O−CH), 23.2 (*Me*−C═N), 18.6, 13.0, 12.9, 12.8, 12.5, 12.1 (Me_{pz}). IR (KBr): ν 2522, 1724.8, 1551.6 cm^{-1}.

Synthesis of 3b. This compound was prepared as indicated for **3a**, starting from **1b** and benzaldehyde (0.04 g, 35% yield). ^1H NMR ($CDCl_3$, 25 °C): δ 7.16 (d, 1H, J_{HH} = 6.5, 1.1 Hz), 6.80 (br m, 2H), 6.67 (t, 1H, J_{HH} = 6.2 Hz) (Ir−C_6H_4), 6.41 (s, 2H), 6.09 (t, 1H, J_{HH} = 8.1 Hz), 5.83 (s, 1H) (N−C_6H_4), 6.05 (s, 1 H, ═CH_2), 5.82 (s, 1 H, ═CH_2), 5.80, 5.34, 5.28 (s, 1 H each, CH_{pz}), 5.25 (s, 1H, O−CH), 3.56 (s, 3H, OMe), 2.41, 2.31, 2.28, 2.21, 1.52, 1.22 (6s, 3H each, $6Me_{pz}$), 1.99 (s, 3H, Me-C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 174.4 (C═N), 160.0 (Ir−C), 158.0 (C−N), 152.1, 151.8, 150.7, 143.5, 143.3, 142.6 (Cq_{pz}), 151.1 (*C*═CH_2), 145.4 (*C*−C(H)O), 141.0 (*C*−OMe), 138.7, 122.8, 122.5, 118.4 (CH, Ir−C_6H_4), 128.9, 123.7, 113.0, 111.8 (CH, N−C_6H_4), 121.5 (CH_2), 107.5, 107.5, 105.9 (CH_{pz}), 87.9 (O−CH), 55.4 (OMe), 23.2 (*Me*−C═N), 18.3, 12.9, 12.8, 12.7, 12.4, 11.9 (Me_{pz}). IR (KBr): ν 2527, 1723.3, 1549.7 cm^{-1}.

Synthesis of 4a. This compound was prepared by following the procedure described for **3a**, from **1a** and *p*-anisaldehyde. Recrystallization was carried out from diethyl ether (0.09 g, 50% yield). ^1H NMR ($CDCl_3$, 25 °C): δ 7.14 (d, 1H, J_{HH} = 8.0 Hz), 6.47 (dd, 1H, J_{HH} = 7.7, 2.6 Hz), 6.44 (d, 1H, J_{HH} = 2.2 Hz) (Ir−C_6H_3), 6.97 (dd, 1H, J_{HH} = 8.4, 2.6 Hz), 6.65 (dd, 1H, J_{HH} = 9.0, 2.3 Hz), 6.53 (dd, 1H, J_{HH} = 8.6, 2.8 Hz), 5.93 (dd, 1H, J_{HH} = 8.8, 2.6 Hz) (C_6H_4), 6.11 (s, 1H, ═CH_2), 5.91 (s, 1H, ═CH_2), 5.86, 5.41, 5.39 (s, 1 H each, CH_{pz}), 5.16 (s, 1H, O−CH), 3.63 (s, 3H, OMe), 2.49, 2.42, 2.37, 2.28, 1.65, 1.40 (6s, 3H each, 6 Me_{pz}), 2.04 (s, 3H, Me-C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 175.4 (C═N), 155.1 (Ir−C), 151.7, 151.6, 150.7, 143.8, 143.3, 142.7 (Cq_{pz}), 153.3 (C−N), 152.1 (*C*═CH_2), 150.4 (*C*−C(H)O), 142.5 (*C*−OMe), 132.1 (C−Cl), 124.1, 118.5, 108.4 (CH, Ir−C_6H_3), 128.3, 128.2, 126.6, 124.1 (CH, N−C_6H_4), 121.3 (CH_2), 107.8, 107.6, 106.1 (CH_{pz}), 88.1 (O−CH), 55.4 (OMe), 23.0 (*Me*−C═N), 18.7, 13.0, 12.9, 12.7, 12.4, 12.1 (Me_{pz}). IR (KBr): ν 2528.6, 1722.8, 1580.5 cm^{-1}.

Synthesis of 4b. This derivative was synthesized by following the procedure described above for **3a**, starting from **1b** and anisaldehyde (0.024 g, 29% yield). ^1H NMR ($CDCl_3$, 25 °C): δ 7.14 (d, 1H, J_{HH} = 7.7 Hz), 6.53−6.43 (dd and d, 2H) (Ir−C_6H_3), 6.53−6.43 (2d, 2H), 6.18 (d, 1 H, J_{HH} = 9.2 Hz), 5.90 (d, 1 H, J_{HH} = 9.5 Hz) (C_6H_4), 6.07 (s, 1 H, ═CH_2), 5.88 (s, 1 H, ═CH_2), 5.86, 5.42, 5.36 (s, 1 H each, CH_{pz}), 5.18 (s, 1 H, O−CH), 3.66, 3.65 (s, 3 H each, 2 OMe), 2.48, 2.42, 2.37, 2.29, 1.64, 1.40 (s, 3 H each, 6 Me_{pz}), 2.07 (s, 3 H, Me-C═N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 174.4 (C═N), 157.9 (C−N), 155.1 (Ir−C), 153.5 (*C*−C(H)O), 152.1, 151.8, 150.6, 143.5, 143.2, 142.5 (Cq_{pz}), 151.9 (*C*═CH_2), 145.6, 143.1 (*C*−OMe), 124.0, 118.5, 108.3 (CH, Ir−C_6H_3), 128.3, 123.8, 113.1, 111.9 (CH, N−C_6H_4), 120.7 (CH_2), 107.9, 107.5, 106.0 (CH_{pz}), 88.0 (O−CH), 55.6, 55.5 (OMe), 23.2 (*Me*−C═N), 18.5, 13.0, 12.9, 12.8, 12.5, 12.2 (Me_{pz}). IR (KBr): ν 2525.2, 1728.1, 1579.0 cm^{-1}.

X-ray Structure Analyses for Compounds 3a and 3b. An X-ray-quality red crystal was glued onto the tip of a glass fiber, and reflections were collected on a Bruker-SMART 5000 CCD-based diffractometer, using ω scans and a rotating anode with Mo Kα radiation (λ = 0.710 73 Å) at room temperature. The frames were integrated with the SAINT software package,[22] using a narrow-frame algorithm, and the structure was solved by direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures with SHELXTL 5.1.[23] The structure was checked with PLATON[24] or SXGRAPH included in the WINGX VI.6[25] crystallographic software package. Non-H atoms were refined with anisotropic thermal parameters. Hydrogen atoms were treated as idealized contributions. Pertinent crystallographic data are collected in Table 1.

Acknowledgment. Financial support from the CONACYT (Grant No.s I32816-E, I32816), the "Ricardo J. Zevada" Foundation, and the Cooperation project CSIC-CONACYT (Grant No. 2004MX0023) are very gratefully acknowledged. Dr. M. Paneque is gratefully acknowledged for useful suggestions and discussions.

Supporting Information Available: CIF files giving details for the crystal structure determinations of **3a** and **3b** and figures giving a ^1H NMR spectrum of the crude product of the reaction leading to **4a** and ^1H, $^{13}C\{^1H\}$, HMQC, and HMBC spectra for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050582Z

(22) Bruker AXS. SAINT, Area Detector Control Software; Bruker Analytical X-ray Systems, Madison, WI, 1995.

(23) Sheldrick, G. M. SHELXTL 5.1, Program for Structure Solution and Least Squares Refinement; University of Göttingen, Göttingen, Germany, 1998.

(24) (a) Speck, A. L. *Acta Crystallogr.* **1990**, *A46*, C34. (b) Speck, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2001.

(25) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.