ORGANOMETALLICS
Organometallics, 1996, 15(1), 16-18, DOI:10.1021/om950756k

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[ArN][$(F_3C)_2$MeCO]Mo=C(t-Bu)-P(OCMe$(CF_3)_2$)-C(H)(t-Bu) **3**. Under an argon atmosphere (glove box), a 25 mL scintillation vial was charged with a magnetic stir bar, 0.075 g (0.107 mmol) of [ArN][$(F_3C)_2$MeCO]$_2$Mo=C(H)(t-Bu) (**2**), and 1.0 mL of dry Et_2O. At 25 °C, 12 μL (0.128 mmol) of t-butylphosphaacetylene (**1**) was added and the vial was capped; the catalyst solution changed from yellow to red-orange. After stirring 5 h, solvent removal under vacuum left a orange residue which was dissolved in a minimum of dry pentane. Cooling at -40 °C yielded 0.075 g of orange crystals (87% yield based on starting molybdenum alkylidene **2**).

Spectroscopic data for **3**: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.01 (s, 3H, [(2,6-(i-Pr)$_2C_6H_3$)N]Mo), 4.72 (d, 1H, $^2J_{P-H}$ = 7 Hz, Mo-C(*H*)(C$(CH_3)_3$), 3.76 (septet, 2H, $^3J_{H-H}$ = 7 Hz, [(2,6-(*i-Pr*)$_2C_6H_3$)N]Mo), 1.75 (s, 3H, P(OCC*H*$_3(CF_3)_2$)), 1.38 (s, 3H, [$(F_3C)_2$C*H*$_3$CO]Mo), 1.35 (s, 9H, Mo(=C(C(C*H*$_3)_3$))), 1.32, 1.16 (each a d, 12H, $^3J_{H-H}$ = 7 Hz, [(2,6-(*i-Pr*)$_2C_6H_3$)N]Mo), 0.91 (s, 9H, Mo-C(H)(C(C*H*$_3)_3$)). ^{13}C NMR (75 MHz, C_6D_6): δ = 251.9 (d, $^1J_{P-C}$ = 85 Hz, Mo(=*C*(C$(CH_3)_3$), 154.1, 145.2, 128.3, 123.6 ([(2,6-(i-Pr)$_2C_6H_3$)N]Mo), 124.0, 122.9 (q, $^1J_{C-F}$ = 284 Hz, P(OCCH$_3$(*C*F$_3)_2$), [$(F_3C)_2$CH$_3$CO]Mo), 120.4 (d, $^2J_{C-P}$ = 69 Hz, Mo-*C*(H)(C$(CH_3)_3$), 80.6 (septet, $^2J_{C-F}$ = 29 Hz, [$(F_3C)_2$CH$_3$*C*O]Mo), 78.5 (doublet of septets, $^2J_{C-F}$ = 30 Hz, $^2J_{P-C}$ = 4 Hz, P(O*C*CH$_3(CF_3)_2$), 45.8 (d, $^2J_{C-P}$ = 25 Hz, Mo(=C(*C*(CH$_3)_3$))), 38.2 (d, $^2J_{C-P}$ = 17 Hz, Mo-C(H)(*C*(CH$_3)_3$)), 33.4, 33.3 (both doublets, $^3J_{C-P}$ = 15 Hz, 18Hz, Mo(=C(C(*C*H$_3)_3$)) and Mo-C(H)(C(*C*H$_3)_3$)), 28.2, 24.3, 23.9 (all singlets, [(2,6-(*i-Pr*)$_2C_6H_3$)N]Mo), 18.8 (s, [$(F_3C)_2$*C*H$_3$CO]Mo), 15.3 (d, $^1J_{P-C}$ = 21 Hz, P(OCCH$_3(CF_3)_2$)). ^{31}P NMR (121.4 MHz, C_6H_6, ext. H_3PO_4): δ = -105.7 (s). IR (C_6D_6): ν = 2962, 2927, 2868, 1261, 1216, 1172, 1088, 1015, 870 cm^{-1}. Anal. Calcd for $C_{30}H_{42}NO_2F_{12}PMo$: C, 44.84; H, 5.27; N, 1.74. Found: C, 45.05; H, 5.19; N, 1.79.

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STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_{30}H_{42}NO_2F_{12}PMo$
Color; Habit	Orange prism
Crystal size (mm)	0.23 x 0.33 x 0.36
Crystal System	Monoclinic
Space Group	$P2_1$
Unit Cell Dimensions	$\underline{a}$ = 9.6300(13) Å
	$\underline{b}$ = 14.9585(14) Å
	$\underline{c}$ = 12.9448(13) Å
	β = 110.120(11)°
Volume	1750.9(3) $Å^3$
Z	2
Formula weight	803.6
Density(calc.)	1.524 Mg/m^3
Absorption Coefficient	0.512 mm^{-1}
F(000)	820

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Data Collection

Diffractometer Used	Siemens P4
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	163
Monochromator	Highly oriented graphite crystal
2θ Range	4.0 to 45.0^{o}
Scan Type	θ–2θ
Scan Speed	Constant; 3.00^{o}/min. in ω
Scan Range (ω)	1.20^{o} plus Kα-separation
Background Measurement	Estimated from 96 step profile
Standard Reflections	3 measured every 97 reflections
Reflections Collected	2558
Independent Reflections	2396 (R_{int} = 1.2%)
Observed Reflections	2258 ($F > 4.0\sigma(F)$)
Absorption Correction	N/A

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Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	$\eta = 0.7(2)$
Extinction Correction	N/A
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Number of Parameters Refined	278
Final R Indices (obs. data)	$R_F = 3.0\%$, $R_{wF} = 3.5\%$
Goodness-of-Fit	1.64
Largest and Mean Δ/σ	0.002, 0.001
Data-to-Parameter Ratio	8.1:1
Largest Difference Peak	0.36 $e\text{Å}^{-3}$
Largest Difference Hole	-0.31 $e\text{Å}^{-3}$

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Table 2. Atomic coordinates ($x10^5$) and equivalent isotropic displacement coefficients ($Å^2 x10^4$)

	x	y	z	U(eq)
Mo(1)	-7897(5)	50000	-24511(3)	190(2)
P(1)	-26821(16)	62504(13)	-25115(12)	216(5)
N(1)	6079(49)	44989(36)	-13576(37)	224(18)
O(1)	-8295(43)	46395(30)	-38924(30)	250(14)
O(2)	-34639(41)	64663(30)	-38731(31)	234(14)
C(1)	-29116(54)	50417(59)	-23529(42)	228(11)
C(2)	-34227(65)	47189(41)	-14101(49)	284(15)
C(3)	-24124(64)	51020(61)	-3040(47)	393(16)
C(4)	-50019(62)	49885(69)	-16009(48)	419(14)
C(5)	-33199(81)	36973(50)	-13882(60)	436(18)
C(6)	-7226(61)	62575(42)	-22677(44)	221(14)
C(7)	2189(65)	70779(45)	-18723(48)	281(14)
C(8)	-2974(78)	78219(52)	-27297(56)	415(18)
C(9)	985(68)	74180(48)	-7873(49)	325(15)
C(10)	18300(70)	68444(54)	-16929(58)	394(18)
C(11)	18672(60)	40891(42)	-6158(44)	209(13)
C(12)	25711(66)	44556(43)	4462(49)	258(14)
C(13)	37847(73)	40028(49)	11317(54)	319(16)
C(14)	43034(79)	32262(51)	8171(56)	409(17)
C(15)	36194(67)	28891(48)	-2155(50)	337(16)
C(16)	24006(65)	33160(44)	-9650(48)	255(14)
C(17)	20471(67)	52924(42)	8404(49)	304(16)
C(18)	14910(66)	50695(68)	17890(47)	424(16)
C(19)	32785(91)	59995(61)	11949(69)	560(23)
C(20)	16461(67)	29370(46)	-21058(51)	280(15)
C(21)	26981(78)	24082(57)	-25417(60)	475(19)
C(22)	3434(83)	23818(58)	-21538(64)	545(21)
C(23)	-6372(56)	49252(55)	-48617(41)	263(13)
C(24)	8633(76)	45565(51)	-48319(56)	371(17)
C(25)	-19028(76)	45173(51)	-58068(54)	369(17)
C(26)	-6407(79)	59323(52)	-49683(60)	441(19)
C(27)	-48755(65)	68595(43)	-43689(47)	239(14)
C(28)	-46144(78)	78094(52)	-46718(57)	393(17)
C(29)	-55999(75)	62993(51)	-54189(57)	383(17)
C(30)	-58784(70)	68450(50)	-36880(53)	380(17)

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F(1)	9483(45)	36789(32)	-47159(32)	513(17)
F(2)	19449(38)	49084(46)	-39934(30)	622(17)
F(3)	11471(43)	47493(36)	-57460(31)	592(20)
F(4)	-18268(45)	47603(34)	-67882(26)	572(19)
F(5)	-31917(38)	47821(37)	-57788(31)	574(19)
F(6)	-18965(46)	36412(32)	-58002(34)	525(18)
F(7)	-41438(48)	83128(30)	-37611(34)	511(18)
F(8)	-36007(45)	78755(34)	-51488(34)	549(18)
F(9)	-58523(47)	81955(32)	-53415(34)	550(18)
F(10)	-56436(42)	54431(32)	-51654(38)	557(17)
F(11)	-48636(49)	63627(35)	-61143(30)	591(18)
F(12)	-69887(43)	65581(39)	-59494(36)	729(21)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

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Table 3. Interatomic Distances (Å)

Mo(1)-P(1)	2.594(2)	Mo(1)-N(1)	1.751(4)
Mo(1)-O(1)	1.930(4)	Mo(1)-C(1)	2.092(6)
Mo(1)-C(6)	1.894(6)	P(1)-O(2)	1.693(4)
P(1)-C(1)	1.841(9)	P(1)-C(6)	1.803(6)
N(1)-C(11)	1.403(7)	O(1)-C(23)	1.397(7)
O(2)-C(27)	1.416(7)	C(1)-C(2)	1.542(10)
C(2)-C(3)	1.538(8)	C(2)-C(4)	1.509(9)
C(2)-C(5)	1.531(10)	C(6)-C(7)	1.507(9)
C(7)-C(8)	1.529(10)	C(7)-C(9)	1.535(10)
C(7)-C(10)	1.528(9)	C(11)-C(12)	1.417(8)
C(11)-C(16)	1.402(9)	C(12)-C(13)	1.378(8)
C(12)-C(17)	1.503(9)	C(13)-C(14)	1.380(11)
C(14)-C(15)	1.367(9)	C(15)-C(16)	1.394(8)
C(16)-C(20)	1.514(8)	C(17)-C(18)	1.536(10)
C(17)-C(19)	1.537(11)	C(20)-C(21)	1.537(11)
C(20)-C(22)	1.488(11)	C(23)-C(24)	1.535(10)
C(23)-C(25)	1.526(8)	C(23)-C(26)	1.513(11)
C(24)-F(1)	1.321(9)	C(24)-F(2)	1.328(7)
C(24)-F(3)	1.334(9)	C(25)-F(4)	1.347(9)
C(25)-F(5)	1.315(9)	C(25)-F(6)	1.311(9)
C(27)-C(28)	1.518(10)	C(27)-C(29)	1.544(9)
C(27)-C(30)	1.515(11)	C(28)-F(7)	1.340(8)
C(28)-F(8)	1.326(10)	C(28)-F(9)	1.340(8)
C(29)-F(10)	1.326(9)	C(29)-F(11)	1.327(10)
C(29)-F(12)	1.333(8)		

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Table 4. Interatomic Angles (°)

P(1)-Mo(1)-N(1)	132.0(2)	P(1)-Mo(1)-O(1)	113.1(1)
N(1)-Mo(1)-O(1)	114.6(2)	P(1)-Mo(1)-C(1)	44.7(2)
N(1)-Mo(1)-C(1)	117.3(2)	O(1)-Mo(1)-C(1)	111.9(2)
P(1)-Mo(1)-C(6)	44.0(2)	N(1)-Mo(1)-C(6)	109.9(2)
O(1)-Mo(1)-C(6)	112.8(2)	C(1)-Mo(1)-C(6)	87.4(3)
Mo(1)-P(1)-O(2)	103.0(2)	Mo(1)-P(1)-C(1)	53.0(2)
O(2)-P(1)-C(1)	106.0(2)	Mo(1)-P(1)-C(6)	46.9(2)
O(2)-P(1)-C(6)	104.2(3)	C(1)-P(1)-C(6)	98.3(3)
Mo(1)-N(1)-C(11)	169.6(5)	Mo(1)-O(1)-C(23)	144.9(4)
P(1)-O(2)-C(27)	124.4(4)	Mo(1)-C(1)-P(1)	82.3(3)
Mo(1)-C(1)-C(2)	128.5(4)	P(1)-C(1)-C(2)	118.6(5)
C(1)-C(2)-C(3)	110.4(5)	C(1)-C(2)-C(4)	111.4(5)
C(3)-C(2)-C(4)	109.4(6)	C(1)-C(2)-C(5)	106.9(6)
C(3)-C(2)-C(5)	109.8(5)	C(4)-C(2)-C(5)	109.0(6)
Mo(1)-C(6)-P(1)	89.1(3)	Mo(1)-C(6)-C(7)	147.3(4)
P(1)-C(6)-C(7)	122.4(5)	C(6)-C(7)-C(8)	109.8(5)
C(6)-C(7)-C(9)	110.8(6)	C(8)-C(7)-C(9)	108.3(6)
C(6)-C(7)-C(10)	109.0(6)	C(8)-C(7)-C(10)	109.7(6)
C(9)-C(7)-C(10)	109.2(5)	N(1)-C(11)-C(12)	120.5(6)
N(1)-C(11)-C(16)	117.8(5)	C(12)-C(11)-C(16)	121.7(5)
C(11)-C(12)-C(13)	116.8(6)	C(11)-C(12)-C(17)	123.2(5)
C(13)-C(12)-C(17)	120.0(5)	C(12)-C(13)-C(14)	122.5(6)
C(13)-C(14)-C(15)	119.8(6)	C(14)-C(15)-C(16)	121.2(7)
C(11)-C(16)-C(15)	117.9(5)	C(11)-C(16)-C(20)	121.2(5)
C(15)-C(16)-C(20)	120.9(6)	C(12)-C(17)-C(18)	109.9(6)
C(12)-C(17)-C(19)	111.1(6)	C(18)-C(17)-C(19)	110.9(6)
C(16)-C(20)-C(21)	113.3(5)	C(16)-C(20)-C(22)	111.4(6)
C(21)-C(20)-C(22)	110.5(6)	O(1)-C(23)-C(24)	106.4(5)
O(1)-C(23)-C(25)	106.4(5)	C(24)-C(23)-C(25)	111.2(6)
O(1)-C(23)-C(26)	112.9(6)	C(24)-C(23)-C(26)	109.4(6)
C(25)-C(23)-C(26)	110.4(5)	C(23)-C(24)-F(1)	112.4(6)
C(23)-C(24)-F(2)	110.2(6)	F(1)-C(24)-F(2)	107.5(5)
C(23)-C(24)-F(3)	112.2(5)	F(1)-C(24)-F(3)	107.0(6)
F(2)-C(24)-F(3)	107.3(6)	C(23)-C(25)-F(4)	111.1(6)
C(23)-C(25)-F(5)	111.0(6)	F(4)-C(25)-F(5)	107.6(5)
C(23)-C(25)-F(6)	113.2(5)	F(4)-C(25)-F(6)	105.9(6)

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F(5)-C(25)-F(6)	107.7(6)	O(2)-C(27)-C(28)	106.7(5)
O(2)-C(27)-C(29)	104.2(5)	C(28)-C(27)-C(29)	110.2(5)
O(2)-C(27)-C(30)	115.8(5)	C(28)-C(27)-C(30)	111.0(6)
C(29)-C(27)-C(30)	108.6(5)	C(27)-C(28)-F(7)	109.6(6)
C(27)-C(28)-F(8)	113.8(6)	F(7)-C(28)-F(8)	106.7(6)
C(27)-C(28)-F(9)	112.4(6)	F(7)-C(28)-F(9)	106.5(6)
F(8)-C(28)-F(9)	107.5(6)	C(27)-C(29)-F(10)	110.5(5)
C(27)-C(29)-F(11)	111.9(6)	F(10)-C(29)-F(11)	107.8(6)
C(27)-C(29)-F(12)	111.4(6)	F(10)-C(29)-F(12)	107.2(6)
F(11)-C(29)-F(12)	107.8(6)		

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Table 5. Anisotropic displacement coefficients ($Å^2 x 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	199(2)	213(2)	150(2)	-10(3)	49(2)	-5(3)
P(1)	208(8)	257(9)	180(8)	-3(7)	64(6)	6(7)
N(1)	196(26)	273(28)	231(26)	-30(22)	109(22)	-8(23)
O(1)	306(22)	277(22)	192(20)	-4(18)	118(18)	14(17)
O(2)	194(21)	298(25)	201(20)	24(19)	54(17)	31(19)
F(1)	515(25)	624(30)	451(24)	234(22)	234(21)	-16(22)
F(2)	324(19)	1013(39)	429(20)	-261(32)	3(16)	-129(32)
F(3)	520(24)	986(46)	408(22)	-28(25)	335(19)	65(24)
F(4)	648(26)	847(43)	156(17)	-74(25)	55(17)	-28(20)
F(5)	300(20)	846(44)	516(23)	59(22)	65(18)	-114(24)
F(6)	553(26)	521(29)	517(25)	-194(22)	207(22)	-231(22)
F(7)	561(28)	327(23)	596(28)	-10(21)	138(23)	-64(22)
F(8)	538(27)	618(29)	595(27)	42(23)	330(23)	217(23)
F(9)	504(26)	600(30)	497(26)	202(23)	109(22)	287(24)
F(10)	318(22)	454(24)	784(31)	-57(19)	41(21)	-229(23)
F(11)	629(28)	815(34)	266(21)	144(27)	71(20)	-112(23)
F(12)	345(25)	879(39)	658(30)	204(26)	-217(22)	-308(29)

The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

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Table 6. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U
H(3A)	-2745	4909	279	60
H(3B)	-1413	4907	-155	60
H(3C)	-2454	5742	-352	60
H(4A)	-5640	4741	-2283	60
H(4B)	-5301	4776	-1010	60
H(4C)	-5066	5629	-1634	60
H(5A)	-3956	3467	-2082	60
H(5B)	-2318	3521	-1270	60
H(5C)	-3622	3463	-808	60
H(8A)	-222	7617	-3411	60
H(8B)	-1306	7976	-2840	60
H(8C)	319	8338	-2480	60
H(9A)	-913	7564	-897	60
H(9B)	429	6959	-239	60
H(9C)	702	7941	-546	60
H(10A)	1897	6636	-2376	60
H(10B)	2438	7366	-1454	60
H(10C)	2164	6384	-1147	60
H(13A)	4284	4245	1851	60
H(14A)	5137	2923	1328	60
H(15A)	3979	2345	-426	60
H(17A)	1230	5529	244	60
H(18A)	723	4628	1545	60
H(18B)	2300	4834	2392	60
H(18C)	1112	5595	2025	60
H(19A)	3593	6136	585	60
H(19B)	2912	6532	1426	60
H(19C)	4101	5771	1793	60
H(20A)	1292	3431	-2600	60
H(21A)	3524	2778	-2517	60
H(21B)	3043	1900	-2071	60
H(21C)	2202	2209	-3283	60
H(22A)	-316	2733	-1905	60
H(22B)	-166	2183	-2893	60
H(22C)	675	1873	-1681	60

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H(26A)	-1579	6162	-4984	60
H(26B)	131	6178	-4348	60
H(26C)	-477	6097	-5634	60
H(30A)	-5449	7198	-3036	60
H(30B)	-6824	7089	-4115	60
H(30C)	-6002	6241	-3485	60
H(1)	-3503(52)	4802(36)	-3074(40)	18(14)